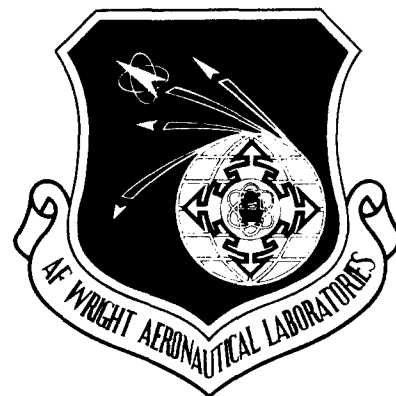


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**HIGH MOLECULAR WEIGHT POLYPHENYLQUINOXALINES WITH INCREASED
SOLVENT RESISTANCE**

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Polymer Branch
Nonmetallic Materials Division

September 1988

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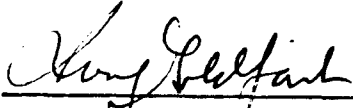
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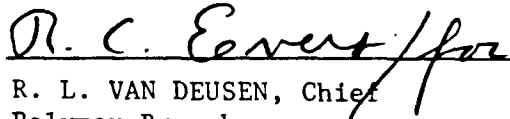
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FOREWORD

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SECTION I

INTRODUCTION

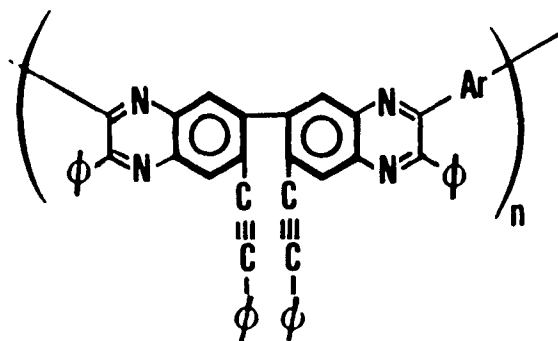
Polyphenylquinoxaline polymers (PPQs) have maintained continued interest over a number of years for their applications as aircraft structural materials. The potential of PPQs for use as metal-to-metal and honeycomb adhesives as well as matrix resins for advanced composites has led to numerous synthetic investigations to produce a variety of polymer backbone structures (Reference 1).

The PPQs in general possess excellent solubility, processability, high-temperature thermoplasticity, and good thermooxidative stability. Although these factors led to excellent processing characteristics, long-term strengths of composites or of adhesive joints at elevated temperatures were adversely affected by high-temperature thermoplasticity (creep). Another adverse property of linear thermoplastic PPQs which prohibits their use in certain aircraft structural applications is their low craze resistance upon exposure to various solvents used in normal aircraft maintenance, such as brake fluid and paint removers.

Attempts to circumvent these problems have been numerous, but two of the most successful efforts in this laboratory have centered around the synthesis of acetylene terminated thermoset oligomers (Reference 2), and IMC curable quinoxaline resins (Reference 3). Acetylene

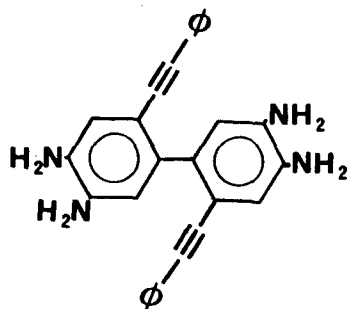
terminated oligomers can be thermally cured without the evolution of volatiles to increase both creep and craze resistance. The oligomers cure via acetylene addition to form a crosslinked polyene network (Reference 4). A second, novel, non-crosslinking approach to the curing of thermoplastic quinoxaline resins involves an intramolecular cycloaddition (IMC) reaction. The IMC reaction introduces a greater degree of chain rigidity by increasing the number of adjacent fused rings along the polymer backbone. This increased rigidity is postulated to increase creep and craze resistance without the formation of a crosslinked network.

IMC polymers cure via the reaction of pendant phenylethynyl groups to form the fused 9-phenyl-dibenz[a,c]-anthracene structure. In previous studies, the 2,2'-bis-(phenylethynyl)biphenyl moieties have been incorporated into both quinoxaline and imide polymer backbones. It was reported that a 120° increase in the final Tg of the polyphenylquinoxaline polymer (1) could be obtained by thermal treatment at



245° for 24 h. This conclusion was based on the observance of a TMA penetration in the cured polymer at 365°. Additional data were necessary to confirm this value since it was in close proximity to the polymer degradation temperature. Further characterization of the polymer was prohibited by the fact that it possessed inadequate flow properties for satisfactory processing. In addition, the molecular weight of the polymer was insufficient for solvent film fabrication, thus prohibiting the acquisition of T_g and mechanical properties data by other methods of analysis.

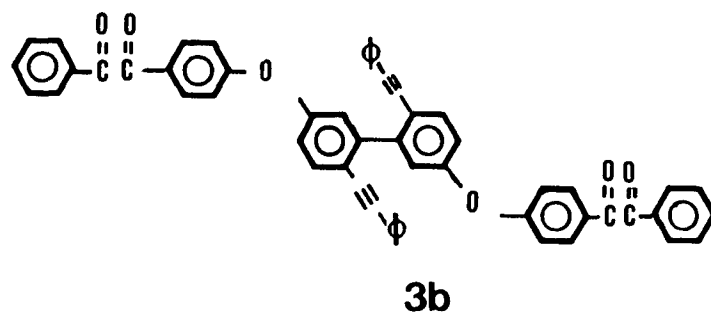
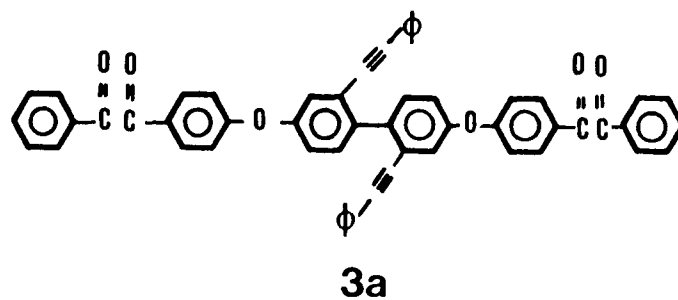
It was considered necessary that larger quantities of higher molecular weight material would be required to carry out the characterization necessary to further investigate the IMC concept. Both the low molecular weight of polymer 1, and difficulties involved in the costly seven step synthesis and subsequent purification of its tetraamine monomer precursor (2), led to the search for a new type of monomer incorporating



2

the 2,2'-bis(phenylethynyl)biphenyl linkage. The objective of

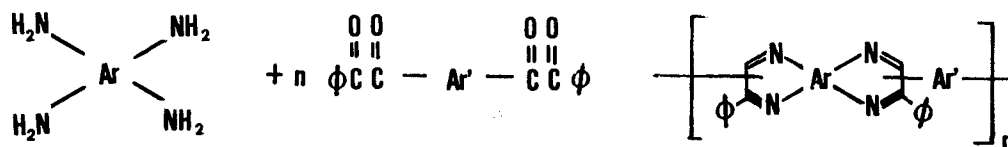
the current work was to synthesize monomers and polymers containing the bis(phenylethynyl) linkage based on the more oxidatively stable and easier to purify bisbenzil monomers 3a and 3b.



SECTION II

RESULTS AND DISCUSSION

Aromatic polyphenylquinoxalines are synthesized by the condensation of aromatic tetraamines with bisbenzil monomers.

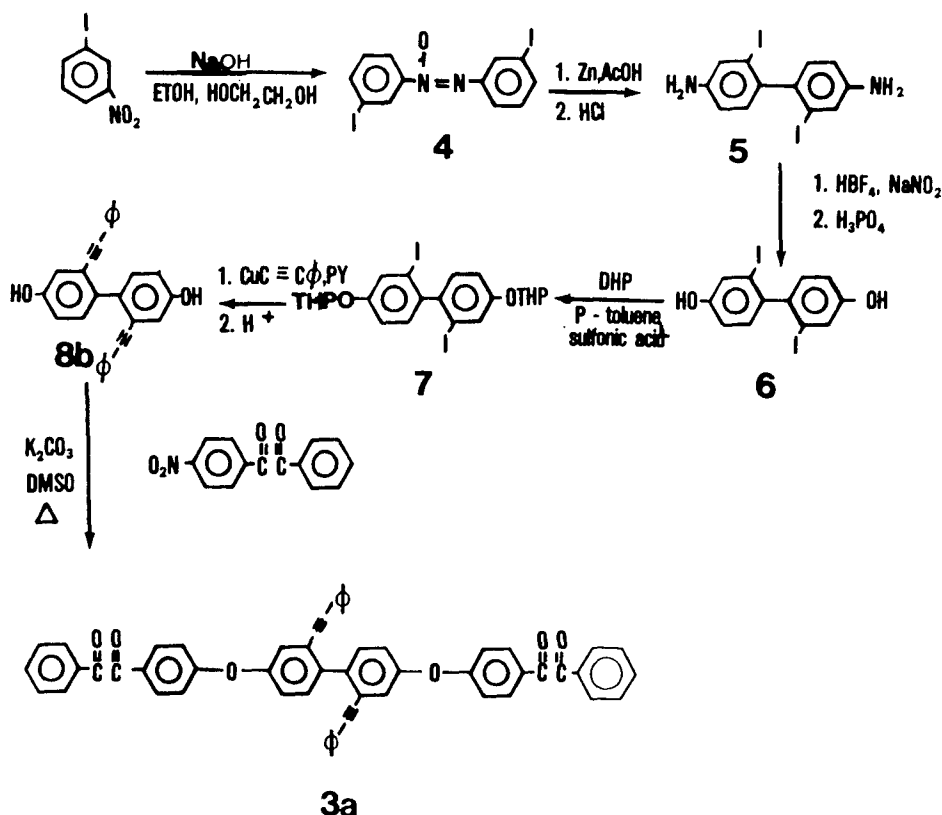


Early efforts to synthesize IMC-containing PPQs focused on attaching pendant groups to tetraamines. It was postulated that the synthesis of bisbenzil monomers containing pendant phenylethynyl groups would offer a more attractive way of incorporating these reactive sites into the polyphenylquinoxaline molecules. Such bisbenzil monomers would be oxidatively stable in air and thus superior to the previously used tetraamine (2). The structures chosen for synthesis were the phenylethynyl containing bisbenzils (3a) and (3b).

1. SYNTHESIS

A. Monomers

The bis-phenylethynyl-substituted tetraketone (3a) was synthesized according to the reaction scheme illustrated below. Treatment of 1-iodo-3-nitrobenzene with potassium hydroxide in a mixture of ethanol and ethylene glycol gave

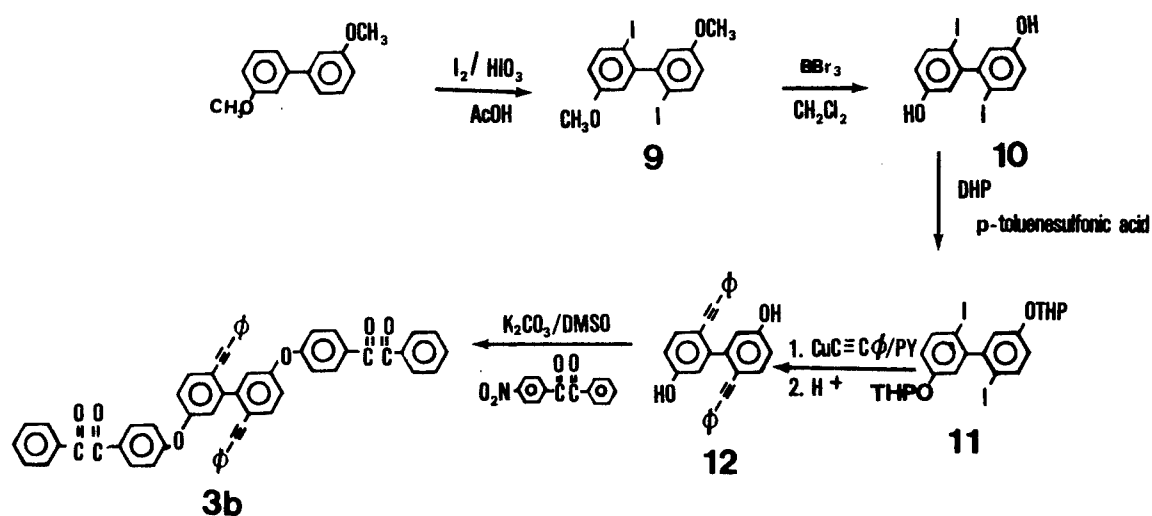


the azoxy compound **4** in 80% yield. The reaction of **4** with zinc dust in acetic acid followed by treatment with concentrated hydrochloric acid produced a 40% yield of the diiodobenzidine (**5**). Diazotization, followed by thermal decomposition of the tetrafluoroborate diazonium salt in aqueous phosphorous acid gave 2,2'-diiodo-4,4'-dihydroxybiphenyl (**6**) in 25% yield after recrystallization. The hydroxy groups were protected in quantitative yield by treating the diphenol **6** with dihydropyran and a catalytic amount of *p*-toluenesulfonic acid to produce **7**. Phenylethynylation of the protected diol using copper phenylacetylide, followed by acidic removal of the tetrahydropyranyl protecting groups

gave the bis-phenylethynylbiphenol (8b) in 50% yield.

Condensation of 8b with two moles of 4-nitrobenzil produced a 65% yield of the tetraketone (3a).

Synthesis of monomer 3b employed a somewhat different synthetic route:



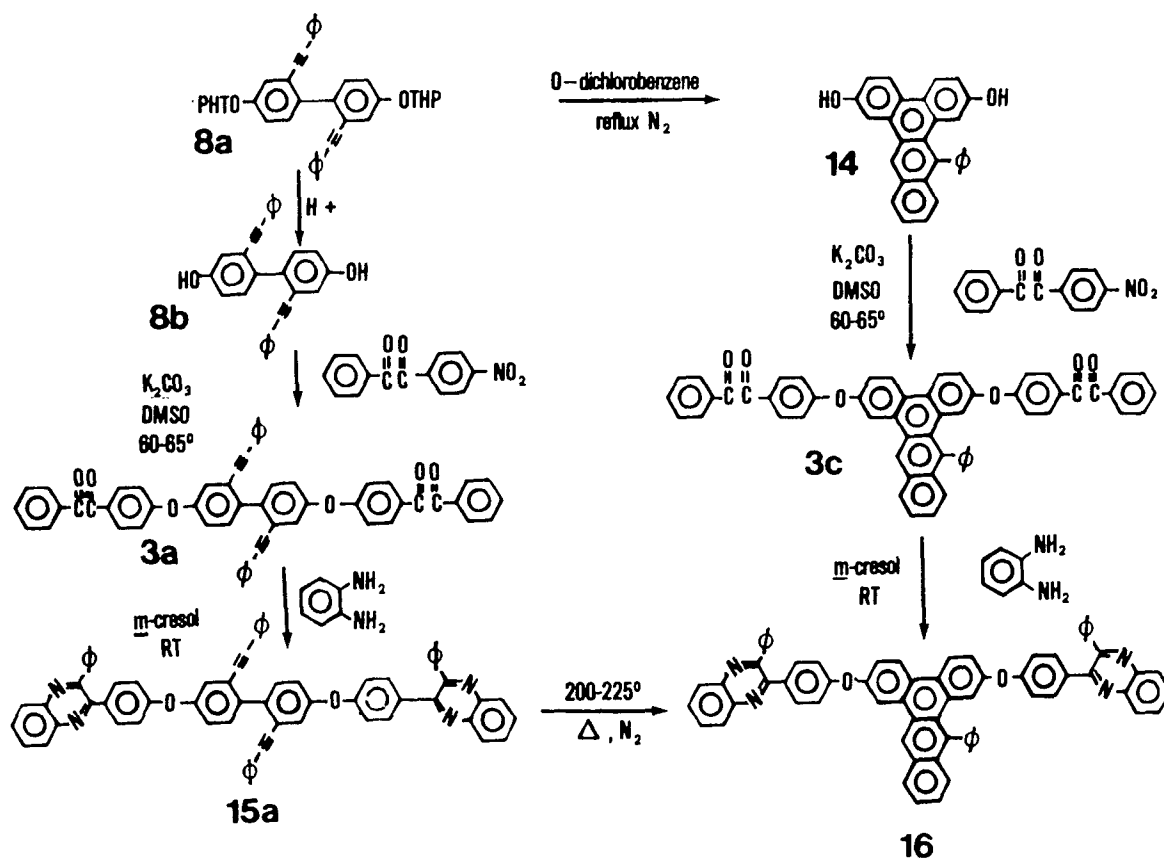
Iodination of 3,3'-dimethoxybiphenyl with iodine in acetic acid afforded, after purification, a 30% yield of the 2,2'-diiodo isomer 9 (Reference 5). Treatment of 9 with boron tribromide in methylene chloride gave the biphenol 10 in high yield. Protection of the hydroxyl functionality proceeded quantitatively using dihydropyran to give 11, and phenylethynylation followed by deprotection gave the diethynyl-bisphenol (12) in 54% yield. The bisbenzil (3b) was obtained in 58% yield via the base catalyzed condensation of 12 with 4-nitrobenzil in DMSO.

In addition to 3a and b, compounds 13a (Reference 6)

and 13b, the bisbenzils without pendant phenylethynyl groups, also were synthesized in order to evaluate the effect of the pendants on polymer properties.

B. Model Compounds

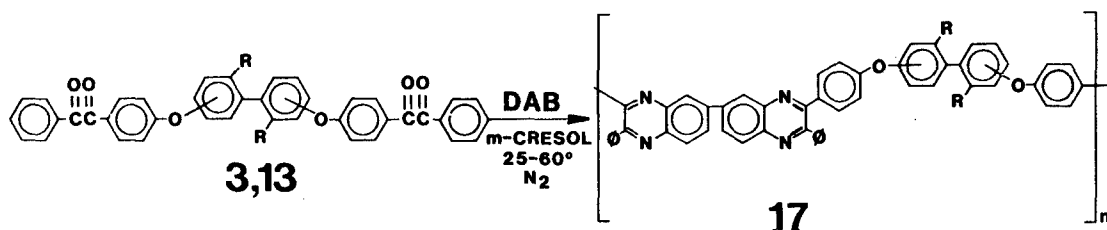
The syntheses of model compounds 15a, 15b, and 16 were carried out to verify monomer purity and to investigate the efficiency of the IMC cyclization reaction. Model compounds 15a and b, formed by the condensation of bisbenzils 3a and b, respectively, with o-phenylenediamine, contained pendant phenylethynyl groups. Compound 16, containing the 9-phenyl-dibenz[a,c]anthracene structure, was synthesized by two



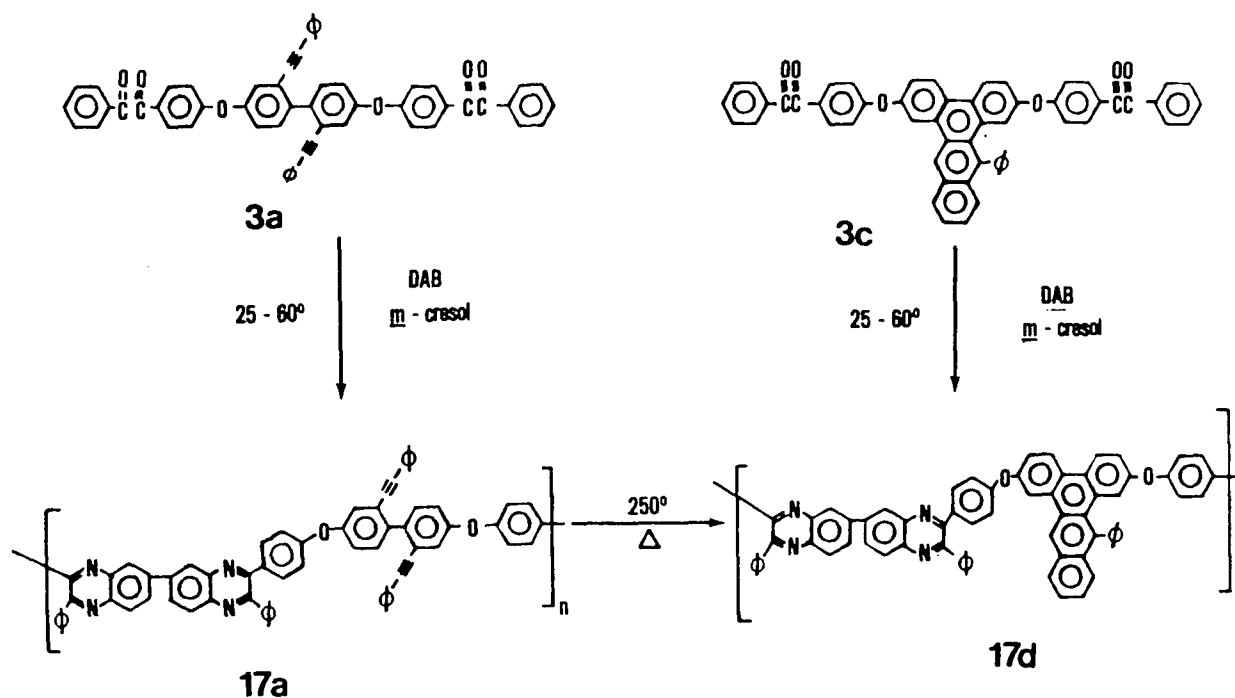
independent routes. The first method involved formation of 2,7-dihydroxy-9-phenyl-benzo[*b*]triphenylene (14) from compound 8b, followed by nitro displacement to form bisbenzil 3c, and then condensation with *o*-phenylenediamine. The second route required heating of model compound 15a to obtain the ring-closed model 16. The two routes led to products which exhibited identical melting points, infrared spectra, and elemental analyses.

C. Polymer Synthesis

The reactions of monomers 13a, 13b, and 3a-c with 3,3'-diaminobenzidine (DAB) were carried out at 5% w/v in a 1:1 mixture of chloroform and *m*-cresol. Stoichiometric amounts of



each bisbenzil and DAB were stirred at room temperature for 20 hours and then heated at 60° for 4 additional hours. For polymers 17a, b, c, and e (Table 1), the resulting viscous solutions were diluted with chloroform and precipitated into methanol. Reprecipitation from chloroform-methanol afforded purified polymers which gave acceptable elemental analyses. Attempts to polymerize monomer 3c, which contained the benz-[*a,c*]anthracene linkage, led to formation of a gel which was



completely insoluble in all solvents investigated.

2. Properties

A. Solubility and Viscosity

Polymers 17a, b, c, and e were soluble in chloroform, m-cresol, and chlorinated aromatic solvents in concentrations greater than 20%. Tough, transparent films could be cast from 2-percent solutions in chloroform.

Thermal cure of films cast from phenylethynylated polymers 7a and b at 193°C gave materials which were not soluble in any common organic solvents or acids. The nature of the rigid 9-phenyldibenzanthracene structure generated during the IMC reaction, rather than interchain crosslinking, is postulated to be the reason for this insolubility. This theory was supported

by the rapid formation of an insoluble gel when the closed bisbenzil 3c was reacted with DAB. In addition, the cured polymers did not have the brittleness that would be associated with a crosslinked system.

Viscosity measurements for some of the soluble polymer samples gave anomalous results. Polymers 17c and e, the materials without pendant groups, exhibited normal viscosity behavior; however, the phenylethynylated polymers, 17a and b, showed dramatic increases in inherent viscosities as the dilution of the samples increased. This behavior was observed in m-cresol, chloroform, and o-dichlorobenzene, and it made the calculation of intrinsic viscosities by the standard procedure impossible. Inherent viscosities values of 0.41 to 1.44 dl/g (0.28 g/dl in m-cresol at 30°) were measured for all of the soluble polymer samples. Viscosity and thermal data for the polymers is summarized in Table 2.

B. Spectral Properties

The bisbenzil, model compound, and polymer structures were investigated by infrared and proton NMR spectroscopy. NMR spectra of the monomers and model compounds contained only aromatic protons, with the closed samples, 3c and 16, exhibiting the expected 9.1 δ peak found in benzo[b]triphenylenes (Reference 7). Infrared data proved to be more valuable for observing changes in structure brought about by the presence or

absence of the IMC pendant groups, and for examining the cure reaction.

Two absorption bands, at 756 and 956 cm^{-1} , were of particular interest because they only were present in the spectra of compounds containing the phenylethynyl group. FTIR scans in the 700-1000 cm^{-1} region clearly indicated that these bands, which were observed in the spectrum of the phenylethynylated polymer (17a), were not present in either the thermally cured material or the polymer without pendants, 17c (Figure 1). In addition, it was possible to follow the change in intensity of these peaks during the thermal cure of a thin film of polymer 17a at 193°C (Figure 2). The superimposed spectra over the 150 minute heating time clearly showed the disappearance of the peaks at the wavelengths of interest.

Spectral data also supported the theory that the cure proceeded by an intramolecular cyclization as opposed to an intermolecular crosslinking reaction. This support came from a comparison of the infrared spectra of a polymer known to contain the 9-phenyldibenzanthracene linkage (17d) with a cured film of polymer 17a, which revealed no appreciable differences between the two scans.

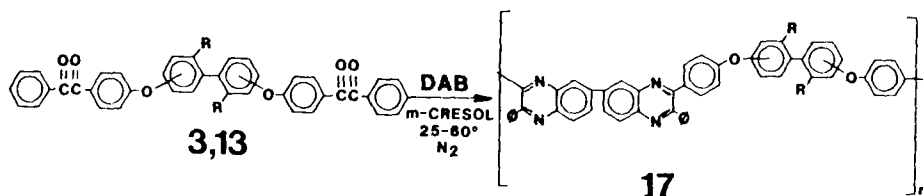
C. DSC and Kinetic Results

The DSC thermogram ($\Delta = 20^\circ/\text{min}$) of polymers 17a and b showed no initial baseline shift characteristic of a glass transition, with exotherm onsets at 190° and 193°C respective-

ly (Table 2). The maxima of each exotherm were reached at 233° and 241°C respectively. In each case, the extrapolated onset of the DSC baseline shift was taken as the temperature of the polymerization exotherm.

The DSC scans at five different heating rates also were used to determine an average value for the energy of activation, $E = 33.37$ kcal/mol. This value was used in turn to produce a reaction window plot for 5, 50, and 95% cures (Figure 21) (Reference 8). The reaction window plot was used to determine the amount of time needed at a given temperature to obtain a certain degree of cure completion. For example, at 193°C, it would require 400 minutes to get a 95% cure of polymer 17a. This data and additional DSC results showing residual exotherm which remained in samples after cure indicated that vitrification of the curing polymer prevented even the intramolecular chain rotation required for the IMC reaction to take place. Although the cure reaction was found to be incomplete, it did proceed to a point at which the solvent resistance was increased without sacrificing the toughness of the resin.

TABLE 1. Polyphenylquinoxaline Isomer Structures



Bisbenzil	Polymer	Isomer	R
3a	17a	4,4'	-C≡C-φ
3b	17b	5,5'	-C≡C-φ
13a	17c	4,4'	-H
13b	17e	5,5'	-H

TABLE 2. Viscosity Data and Thermal Behavior of PPQs

Polymer	η_{inh}^a	T_g^b	T_i^c	$T_{max}^{d,e}$	$T_g(cure)^f$
17a	0.91	f	190°	233°	381°
17b	0.43	f	193°	252°	328°
17c	1.44	283°	-	-	-
17d	g	-	-	-	346°
17e	0.41	220°	-	-	-

a. Inherent viscosity (0.28g/dl in m-cresol, 30°).

b. Determined by DSC, 10°C/min under N₂.

c. Temperature at which curing exotherm begins.

d. Maximum of curing exotherm.

e. From rescan after heating to 450°C.

f. Not observed before cure initiation.

g. Insoluble polymer.

SECTION III

EXPERIMENTAL

The 3,3'-diaminobenzidine was recrystallized from water in a nitrogen atmosphere and stored under vacuum (Reference 9). The 4-nitrobenzil was recrystallized from acetic acid and dried to give a product which melted at 138-139°. The polymerization solvent, m-cresol, was distilled prior to use. All other starting materials were used as obtained from the commercial supplier.

3,3'-Diiodoazoxybenzene (4):

Ethanol (500 ml) and sodium hydroxide (172 g) were heated at 70° in a mechanically stirred flask until most of the NaOH dissolved. Ethylene glycol (600 ml) and 1-iodo-3-nitrobenzene (100 g) were added and the reaction mixture was heated at reflux for 2 h. The warm mixture was added to 4 L ice water and stirred for 30 min. The brown solid was filtered, washed with water, and dried to give a 75-80% yield of product, which was used without further purification.

2,2'-Diiodobenzidine (5):

The crude azoxy product 4 (10 g) was dissolved in tetrahydrofuran (50 ml), and 70 ml glacial acetic acid was added. Zinc dust (5.6 g) was slowly added to maintain the reaction temperature below 40°. Following zinc addition, 85% phosphoric acid (10 ml) was added over 15 min to maintain the temperature below 50°. After

stirring for 30 min, the reaction mixture had lightened in color to pale yellow. It was then diluted with 150 ml water and extracted with methylene chloride (2 x 75 ml). The organic phase was filtered to remove zinc solids and then was added dropwise to a solution of 30 ml concentrated HCl at -5° . The addition took 20 min, with the temperature maintained below 0° throughout. The reaction mixture was filtered, and the white solid was dissolved in hot water (500 ml). The water was filtered and neutralized with ammonium hydroxide to precipitate the product. Recrystallization from toluene gave a 40% yield of 5, mp $167-168^{\circ}$.

4,4'-Dihydroxy-2,2'-diiodobiphenyl (6):

Glacial acetic acid (200 ml) and compound 5 (20.0 g, 49 mmol) were stirred at room temperature for 20 min, and then 100 ml 48% tetrafluoroboric acid was added to the solution. After 30 min, the acidic solution was cooled to -5° , and a sodium nitrite solution (7.2 g NaNO_2 in 80 ml water) was slowly added to maintain the temperature below 0° . The reaction was stirred for 1 h at 0° , and the precipitate which formed was filtered and dried for 18 h under vacuum. The dried product was added over a period of 1 h to a solution of 2L water containing 30 ml phosphorous acid at 75° . Nitrogen was evolved, and heating continued until the evolution of gas was complete (approx. 30 min). The reaction was cooled to room temperature, the orange product filtered and recrystallized from 3:1 water:ethanol. The white product, 6, mp $171-172^{\circ}$, was

collected in 25% yield. Analysis calc'd for $C_{12}H_8I_2O_2$: C, 32.88; H, 1.83; I, 57.99. Found: C, 33.10; H, 1.76; I, 57.64.

2,2'-Diiodo-5,5'-dimethoxybiphenyl (9):

The diiodo compound 9 is prepared by a known procedure (Reference 6) in which 3,3'-dimethoxybiphenyl (5.0 g, 23.4 mmol), iodine (4.7 g, 18.5 mmol), and glacial acetic acid (50 ml) were heated to 100°. HIO_3 (1.7 g, 9.7 mmol) in 4 ml water then was added dropwise over a 10 min period. After heating at 100° for 2 h, the reaction mixture was cooled and poured into 500 ml of water containing a small amount of sodium bisulfite. The resulting white solid was filtered, washed with water, and air-dried overnight. Recrystallization from hexane and treatment with charcoal gave 3.0 g (28%) of crystals mp 140.5-141°, in agreement with the literature value.

2,2'-Diiodo-5,5'-dihydroxybiphenyl (10):

Compound 9 (10.0 g, 21.5 mmol) was cooled to -78° in a dry ice/acetone bath. Boron tribromide (65ml of 1.0 M soln. in methylene chloride) was quickly added via syringe. The reaction was allowed to warm to room temperature and stir for 16h. It was then added slowly to 300 ml water and was stirred for 1 h, during which time CH_2Cl_2 evaporated, allowing the product to be filtered in suitable purity to be carried to the next step (88% yield, mp 185-187°). Analysis calc'd for $C_{12}H_8I_2O_2$: C, 32.88; H, 1.83; I, 57.99. Found: C, 32.75; H, 1.89; I, 58.10.

Bis(tetrahydropyranyl) adduct of 6, (7):

A mixture of 6 (10.0 g, 22.8 mmol) and dihydropyran (12.5 ml, 137 mmol) was cooled to 10°. A small crystal of p-toluenesulfonic acid was added to the reaction and the cooling bath was removed. As the reaction neared room temperature, an exotherm was noted which caused all of the diol to dissolve. After stirring for 1 h the solution was diluted with 100 ml methylene chloride, washed with 10% aq. NaOH and water, and then dried over magnesium sulfate. The volume of the organic phase was reduced to 30 ml and diluted with 200 ml petroleum ether. A white precipitate formed upon stirring of the solution. The precipitate was collected and air dried to give 90% of 7, mp 105-106°. Analysis calc'd for $C_{22}H_{24}I_2O_4$: C, 43.60; H, 4.04; I, 41.86. Found: C, 43.90; H, 3.96; I, 41.79.

Bis(tetrahydropyranyl) adduct of 10 (11):

The bis(tetrahydropyranyl) adduct 11 was synthesized in essentially quantitative yield by the procedure described for the synthesis of compound 7, mp 112-113°. Analysis calc'd for $C_{22}H_{24}I_2O_4$: C, 43.56; H, 3.96; I, 41.88. Found: C, 43.72; H, 4.10; I, 41.75. Mass Spectrum (EIMS): m/z = 606 (M^+), 85 ($C_5H_9O^+$).

Phenylethynylation of 7 (8a):

A mixture of 7 (5.0 g, 8.25 mmol), copper phenylacetylide (3.39 g, 20.6 mmol), and 100 ml pyridine was purged with nitrogen for 15 min and then heated to reflux for 48 h. After cooling to room

temperature, pyridine was removed from the reaction mixture, and the residue was extracted with petroleum ether in a Soxhlet extractor. The petroleum ether was evaporated to yield an off-white solid, which was chromatographed on a 54 cm x 20 cm silica gel column using 2:1 petroleum ether:ether as eluant. The product fractions were evaporated to dryness to yield 50% of the phenylethynylated product, mp 135-137°. Analysis calc'd for $C_{38}H_{34}O_4$: C, 82.3; H, 6.14. Found: C, 81.95; H, 6.20.

4,4'-Dihydroxy-2,2'-bis(phenylethynyl)biphenyl (8b):

To a mixture of 250 ml methanol and the protected phenylethynyl compound, 8a, (5.0 g, 9.0 mmol) was added 2 ml concentrated HCl. After 1 h, all of the reactant had dissolved and thin layer chromatography indicated that all protecting groups had been cleaved to the diol. The solution was neutralized with sodium bicarbonate, filtered, and evaporated to dryness. The residue was recrystallized from toluene to give a 90% yield of 8b, mp 187°. Analysis calc'd for $C_{28}H_{18}O_2$: C, 87.02; H, 4.69. Found: C, 86.90; H, 4.98.

5,5'-Dihydroxy-2,2'-bis(phenylethynyl)biphenyl (12):

A mixture of 11 (9.60 g, 15.9 mmol), copper phenylacetylide (7.83 g, 47.6 mmol), and 100 ml pyridine was purged with nitrogen for 10 min and then was heated to reflux for 25 h. The dark-brown reaction mixture was placed in an evaporating dish to remove pyridine. The black residue was stirred with 600 ml cold 10% HCl,

and then was extracted with 3 x 200 ml ether. The ether layer was separated, reduced in volume to 200 ml, and diluted with 200 ml ethanol and 200 ml 10% HCl to give a homogeneous solution which was stirred for 1 h to cleave the tetrahydropyran protecting groups. The reaction was cooled with ice and then made basic with 10% NaOH. Extraction with 3 x 300 ml chloroform removed the by-product, and the basic solution was reacidified and extracted with 3 x 300 ml ether. Evaporation of the ether gave a product which was purified by column chromatography using 2:1 ethyl acetate:hexane as eluant. The light-yellow product fractions were air dried to give a 54% yield of 12, mp 162-163°. Analysis calc'd for $C_{26}H_{18}O_2$: C, 87.05; H, 4.66. Found: C, 85.68; H, 4.84. Mass Spectrum (EIMS): $m/z = 386$ (M^+), 285 ($M - C_6H_5C=C^+$).

2,7-Dihydroxy-9-phenylbenzo[b]triphenylene (14):

The 4,4'-dihydroxy compound 8b (0.4 g, 1.0 mmol) was heated at reflux in 15 ml trichlorobenzene under a nitrogen atmosphere. After 18 h, the reaction was cooled, 20 ml petroleum ether was added, and the resulting precipitate was filtered. After vacuum drying, 0.24 g of product, 60% yield, with a melting point of 362° was isolated. Analysis calc'd for $C_{26}H_{18}O_2$: C, 87.05; H, 4.66. Found: C, 86.25; H, 4.85. Mass spectrum (EIMS): $m/z = 386$ (M^+).

4,4'-Bis(phenylglyoxaloylphenoxy)-2,2'-bis(phenylethynyl)-1,1'-biphenyl (3a):

A mixture of 8b (2.5 g, 6.5 mmol), 4-nitrobenzil (3.5 g, 13.6

mmol), and 65 ml dry DMSO was purged with nitrogen for 15 min. The yellow solution was heated to 60°, and anhydrous potassium carbonate (2.2 g, 16.2 mmol) was added. The solution immediately became dark purple. Heating continued for 24 h, then the reaction was cooled to room temperature and precipitated into 300 ml 10% HCl. The yellow product was filtered, dried and chromatographed using 1:1 petroleum ether:methylene chloride as eluant. Product fractions were evaporated to give a 63% yield of 3a, an amorphous yellow solid. Analysis calc'd for C₂₆H₁₄O₆: C, 83.77; H, 4.25. Found: C, 83.87; H, 4.27.

5,5'-Bis(phenylglyoxaloylphenoxy)-2,2'-bis(phenylethynyl)-1,1'-biphenyl (3b):

Bisbenzil 3b was prepared from 12 and 4-nitrobenzil by the same procedure used to obtain 3a. The air-dried solid resulting from precipitation into aq. HCl was chromatographed using 4:3 chloroform:hexane as eluant. The product fractions were evaporated to give a 58% yield of 3b, an amorphous yellow solid. Analysis calc'd for C₂₆H₁₄O₆: C, 83.77; H, 4.27. Found: C, 83.95; H, 4.24. Mass Spectrum (EIMS): m/z = 802 (M⁺), 105 (C₆H₅C=O)⁺.

2,7-Bis(phenylglyoxaloylphenoxy)-9-phenylbenzo[b]triphenylene, (3c):

Bisbenzil 3c was prepared in 71% yield from 14 and 4-nitrobenzil by the same procedure used to obtain 3a. Mass spectrum (EIMS): m/z = 802 (M⁺), 105 (C₆H₅C=O⁺).

4,4'-Bis(phenylglyoxaloylphenoxy)-1,1'-biphenyl (13a):

Bisbenzil 13a was prepared from 4,4'-dihydroxybiphenyl and 4-nitrobenzil by a known procedure (Reference 5). The melting point of 167-169° was in agreement with the literature value.

3,3'-Bis(phenylglyoxaloylphenoxy)-1,1'-biphenyl (13b):

Bisbenzil 13b was prepared from 3,3'-dihydroxybiphenyl and 4-nitrobenzil by the same procedure used to synthesize compound 3a. Elution of the product from a silica gel column was accomplished with 2:1 hexane:methylene chloride to give a 77% yield of 13b, which softened at 40-50°. Analysis calc'd for $C_{40}H_{28}O_6$: C, 79.73; H, 4.32. Found: C, 79.74; H, 4.58.

4,4'-Bis(2-phenylquinoxaline-3-yl-p-phenyleneoxy)-2,2'-bis(phenylethynyl)-1,1'-biphenyl (15a):

The bisbenzil 3a (0.70 g, 0.87 mmol) and o-phenylenediamine (0.20 g, 1.84 mmol) were stirred under nitrogen in 10 ml m-cresol for 18 h. The cresol solution was precipitated into 200 ml methanol, and the resulting solid product was filtered, dissolved in CH_2Cl_2 , and reprecipitated in methanol. The product was dried for 18 h under vacuum to give 0.64 g (91%), mp 108-114°. Analysis calc'd for $C_{62}H_{36}N_4O_2$: C, 86.23; H, 4.47; N, 5.92. Found: C, 84.60; H, 4.61; N, 5.80. Mass spectrum (EIMS): 946 (M^+), 179 ($M - C_6H_5NCC_6H_5$)⁺.

5,5'-Bis(2-phenylquinoxaline-3-yl-p-phenoxy)-2,2'-bis(phenylethynyl)-1,1'-biphenyl (15b):

Model Compound 15b was prepared from bisbenzil 3b and o-phenyl-

enediamine by the procedure used to prepare 15a, giving an 88% yield of product, mp 129-135°. Analysis calc'd for $C_{62}H_{38}N_4O_2$: C, 86.23; H, 4.47; N, 5.92. Found: C, 85.41; H, 4.45; N, 5.80.

2,7-Bis(2-phenylquinoxaline-3-yl-p-phenyleneoxy)-9-phenylbenzo[b]-triphenylene (16):

Method A: Model compound 16 was prepared from bisbenzil 3c and o-phenylenediamine by the procedure used to obtain 15a. Method

B: Model compound 15a was refluxed in 1,2,4-trichlorobenzene for 48 h, and then was purified by repeated extractions with hot petroleum ether (mp 140-148). Analysis calc'd for $C_{62}H_{38}N_4O_2$: C, 85.50; H, 4.40; N, 6.43. Found: C, 84.88; H, 4.65; N, 5.59.

Mass spectrum (EIMS): m/z = 947 (M^+), 179 ($C_6H_5NCC_6H_5$)⁺.

Poly[(2,2'-diphenyl[6,6'-biquinoxaline]-3,3'-diyl)-p-phenyleneoxy[6,6'-bis(phenylethynyl)-4,4'-biphenylene]oxy-p-phenylene] (17a):

A mixture of 3a (0.5345 g, 0.6658 mmol) and 3,3'-diaminobenzidine (0.1427 g, 0.6658 mmol) was dissolved in 6 ml chloroform and purged with nitrogen for 15 min. Distilled m-cresol (6 ml) was purged with nitrogen and then added to the monomers. The reaction mixture became dark red, and after 20 h the viscosity increased to stop stirring. The solution was heated to 60° for 4 h, then was cooled to room temperature and diluted with 40 ml chloroform. The polymer was precipitated into 600 ml methanol, filtered, dissolved in chloroform, and reprecipitated into methanol. After drying under vacuum at room temperature, 17a was obtained in 95% yield, with an inherent viscosity of 0.91 dl/g at 0.2874 g/dl in

m-cresol at 30°. Analysis calc'd for C₂₂H₄₀N₄O₂: C, 86.41; H, 4.27; N, 5.92. Found: C, 85.44; H, 4.34; N, 6.01.

Poly[(2,2'-diphenyl[6,6'-biquinoxaline]-3,3'-diyl)-p-phenyleneoxy[6,6'-bis(phenylethynyl)-3,3'-biphenylene]oxy-p-phenylene], 17b:

Polymer 17b was synthesized in 91% yield using bis(benzil) 3b in a procedure like that described for the synthesis of 17a. The inherent viscosity of the polymer was 0.41 dl/g (conc. = 0.2871 g/dl in m-cresol at 30°). Analysis calc'd for C₂₂H₄₀N₄O₂: C, 86.41; H, 4.24; N, 5.93. Found: C, 84.96; H, 4.32; N, 5.70.

Poly[(2,2'-diphenyl[6,6'-biquinoxaline]-3,3'-diyl)-p-phenyleneoxy(4,4'-biphenylene)oxy-p-phenylene], 17c:

Polymer 17c was synthesized in 94% yield using bisbenzil 13a by the method used to make 17a. The inherent viscosity of the product was 1.44 dl/g (concentration = 0.2710 g/dl in m-cresol at 30°). Analysis calc'd for C₂₂H₃₂N₄O₂: C, 83.87; H, 4.30; N, 7.53. Found: C, 84.47; H, 4.43; N, 7.72.

Poly[(2,2'-diphenyl[6,6'-biquinoxaline]-3,3'-diyl)-p-phenyleneoxy-(9-phenylbenzo[bltriphenylene)-2,7-ylene)oxy-p-phenylene] 17d:

Polymer 17d was synthesized using bisbenzil 3c and 3,3'-diaminobenzidine in chloroform/m-cresol. After 15 min, a gel formed in the reaction and subsequent heating to 60° had no effect. The gel was stirred in methanol and then chopped in a blender. No solvent could be found which would dissolve the polymer. Analysis calc'd for C₂₂H₄₀N₄O₂: C, 86.41; H, 4.24; N, 5.93. Found: C,

84.66; H, 4.27; N, 5.90.

Poly[(2,2'-diphenyl[6,6'-biquinoxaline]-3,3'-diyl)-p-phenyleneoxy-(3,3'-biphenylene)oxy-p-phenylene] 17e:

Polymer 17e was synthesized in 92% yield using bisbenzil 13b by the method used to make 17a. The inherent viscosity of the product was 0.58 dl/g (concentration = 0.2975 g/dl in m-cresol at 30°). Analysis calc'd for $C_{52}H_{32}N_4O_2$: C, 83.87; H, 4.30; N, 7.53. Found: C, 84.33; H, 4.51; N, 7.85.

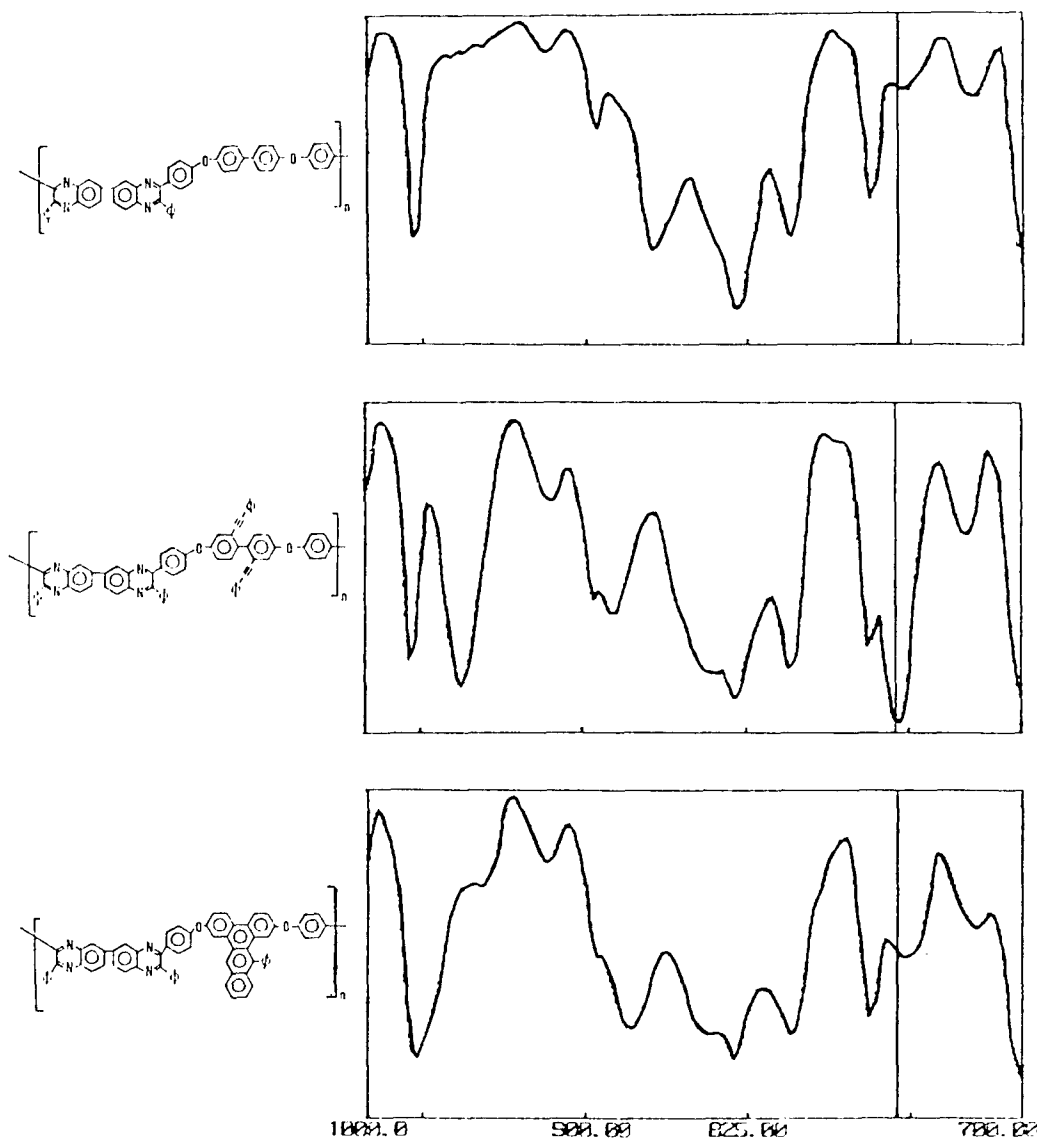


Figure 1. FTIR Comparison Showing Changes in Bending Vibrations with Presence of Phenylethynyl Pendant Groups.

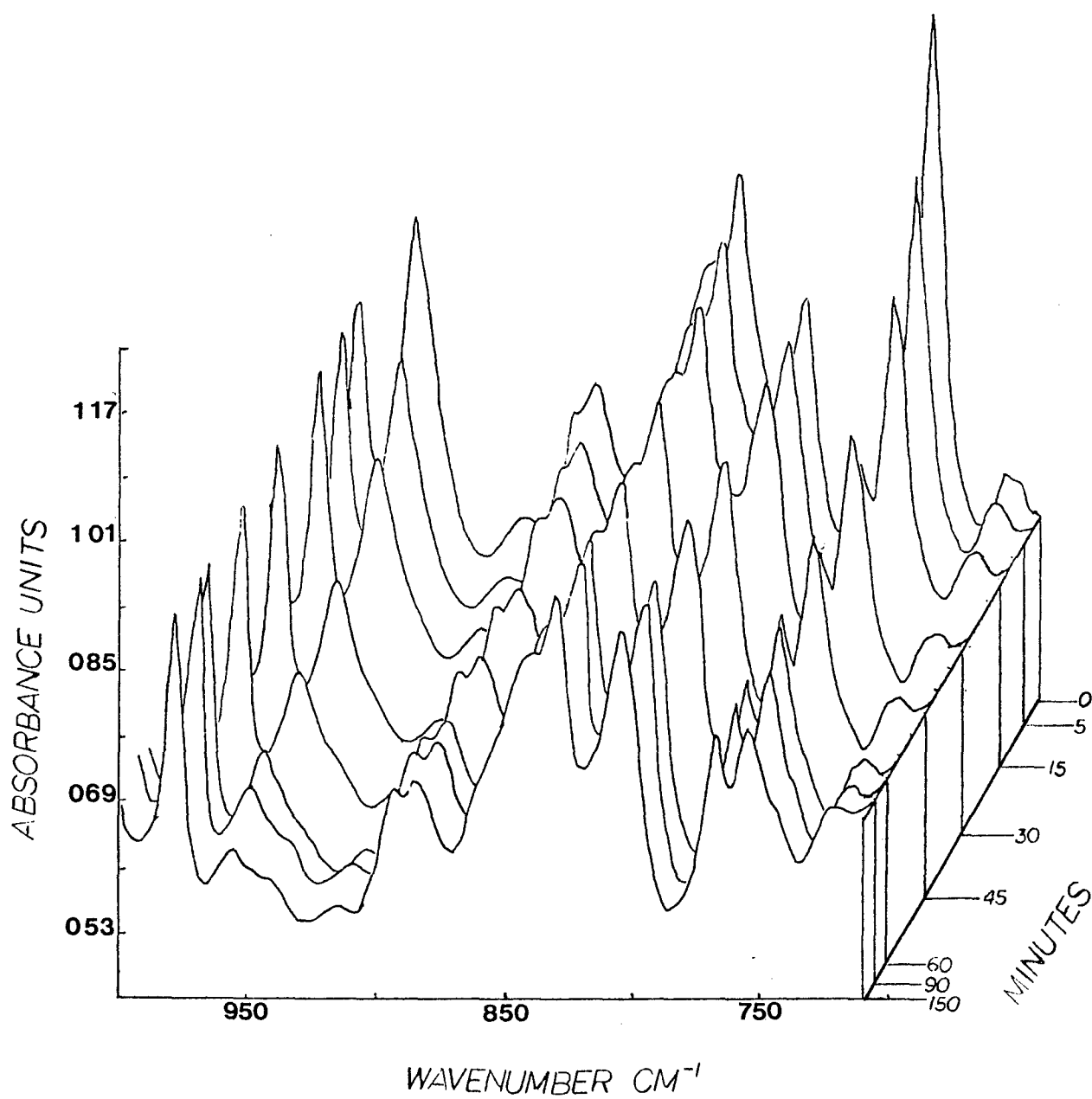


Figure 2. Superimposed FTIR Spectra of the 193°C Cure of Polymer 17a.

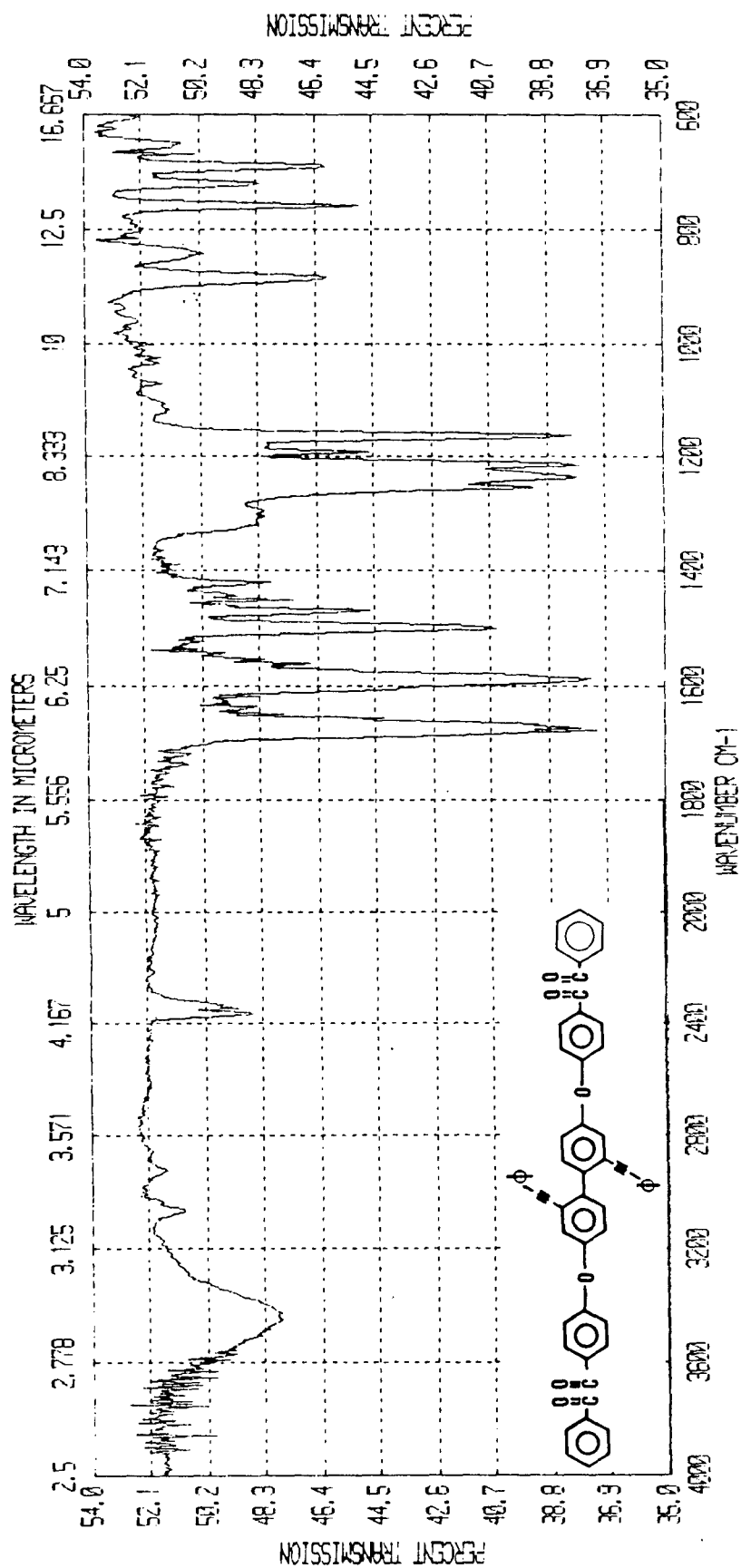


Figure 3. FTIR Spectrum of 4,4'-Bisbenzil Monomer, 3a.

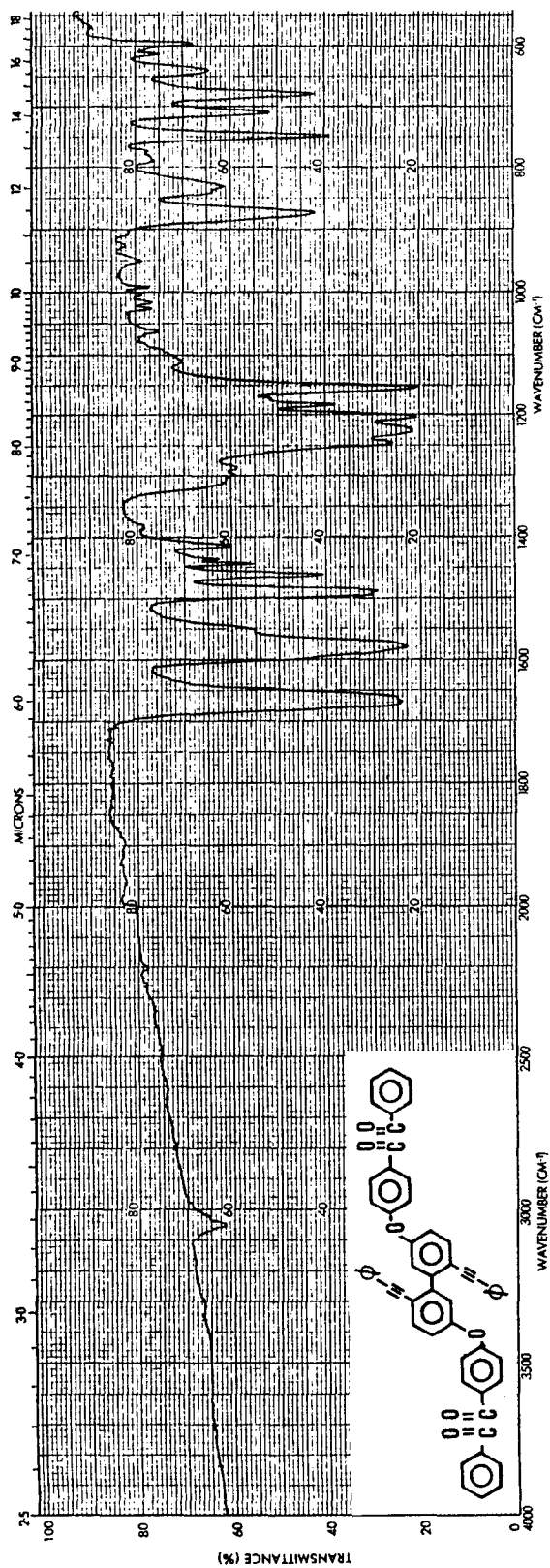


Figure 4. Infrared Spectrum of 5,5'-Bisbenzil Monomer, 3b.

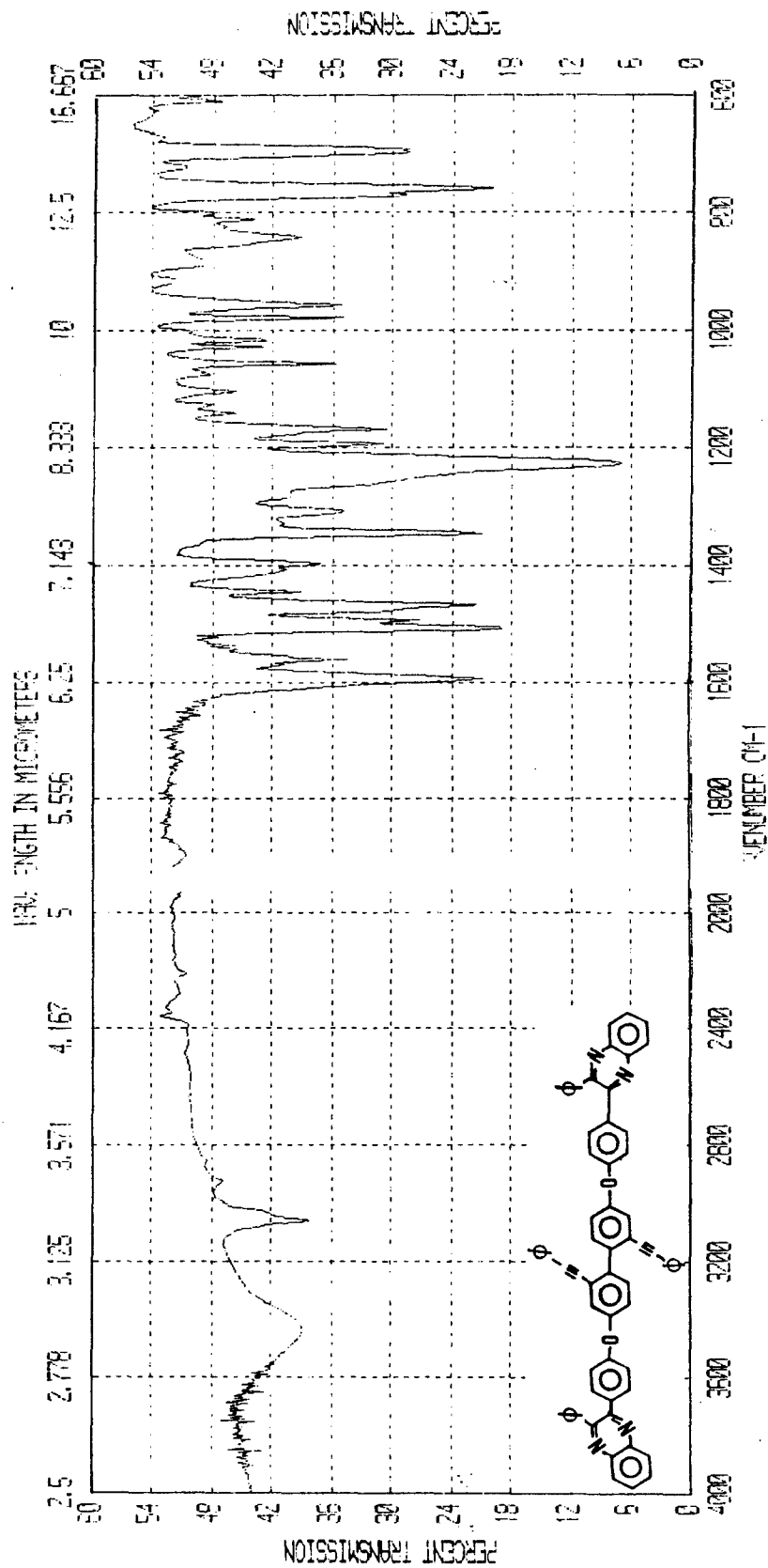


Figure 6. Infrared Spectrum of 4,4'-Quinoxaline Model Compound, 15a.

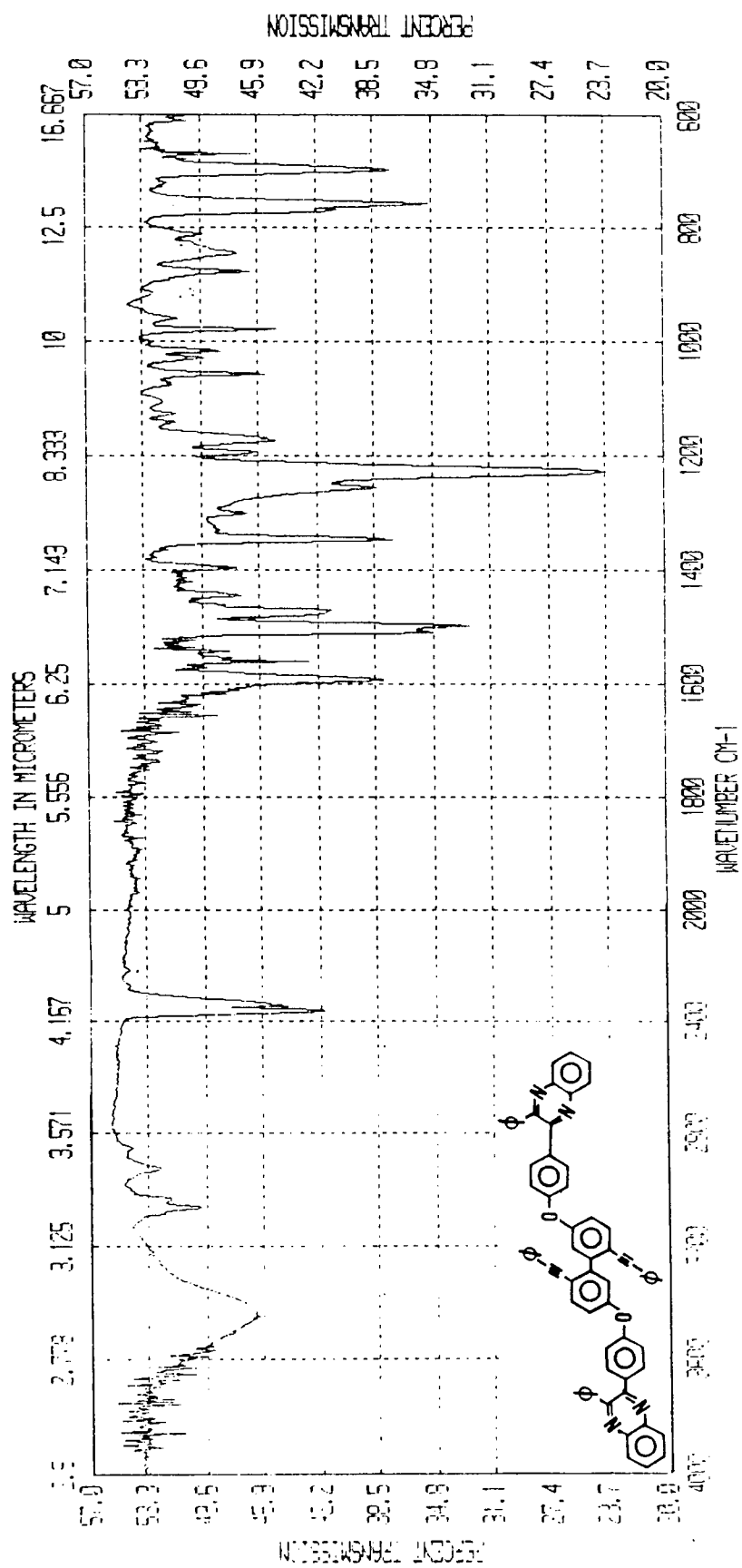


Figure 7. FTIR Spectrum of 5,5'-Quinoxaline Model Compound, 15b.

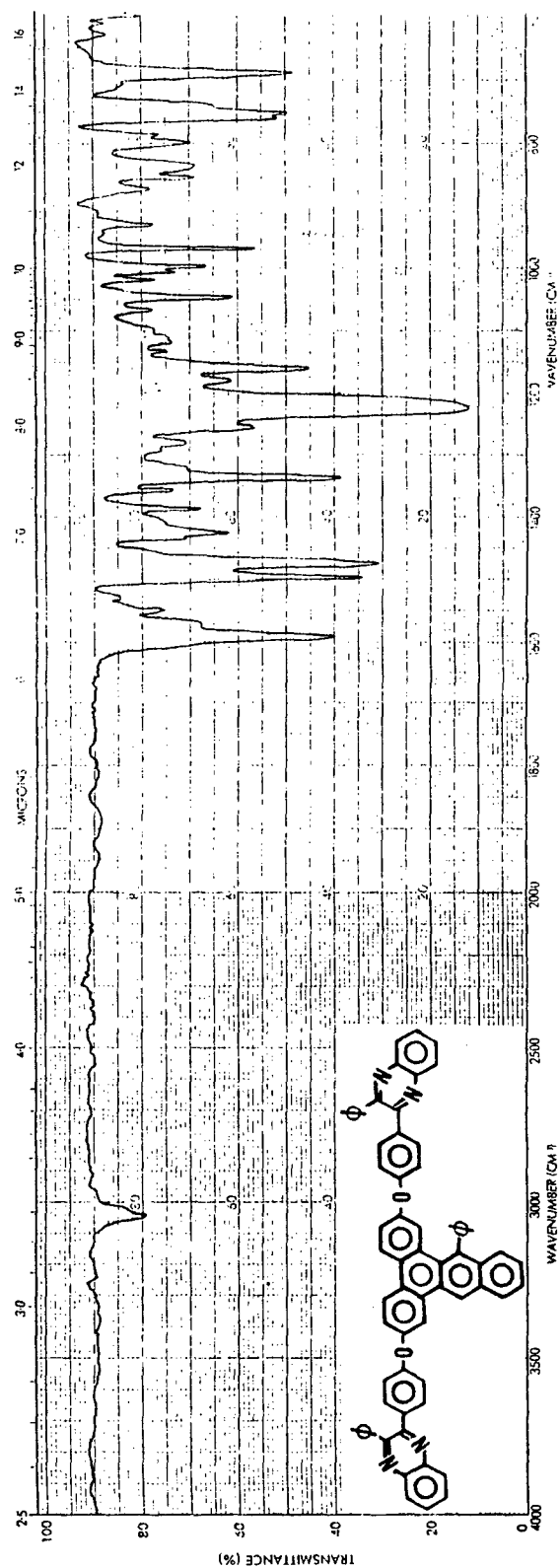


Figure 8. Infrared Spectrum of Closed 4,4'-Quinoxaline Model Compound, 16.

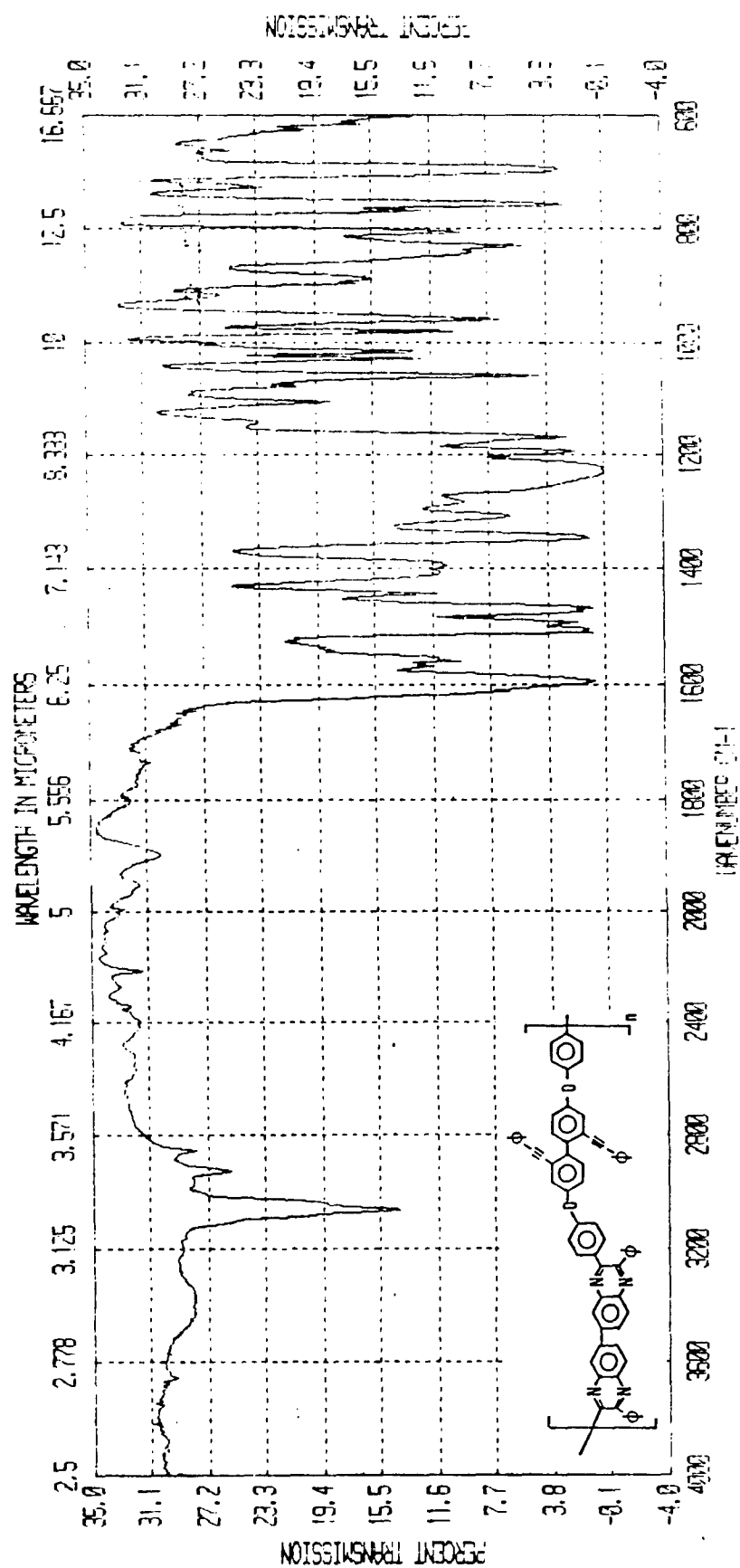


Figure 9. FTIR Spectrum of 4,4'-Quinoxaline Polymer, 17a.

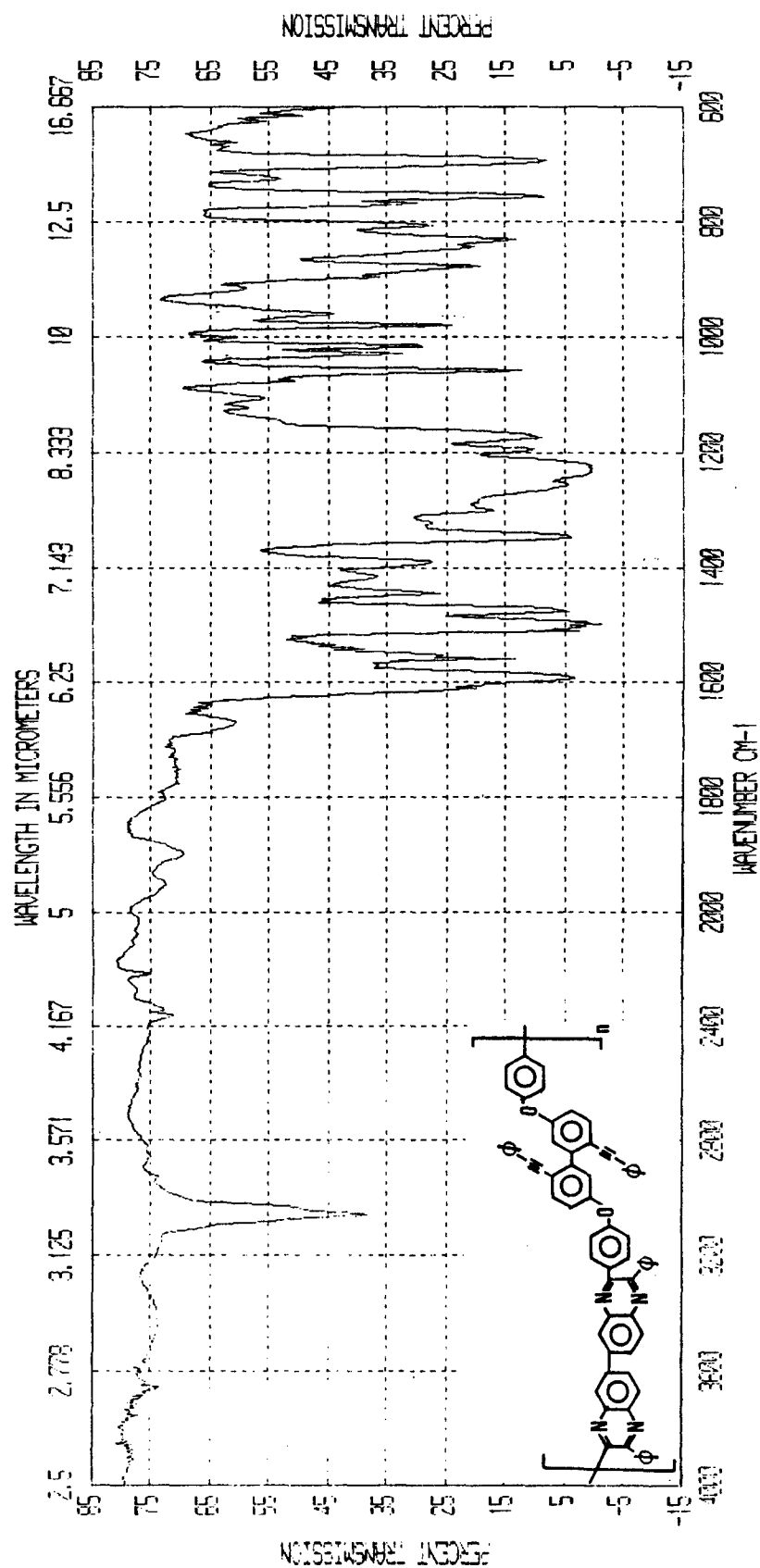


Figure 10. FTIR Spectrum of 5,5'-Quinoxaline Polymer, 17b.

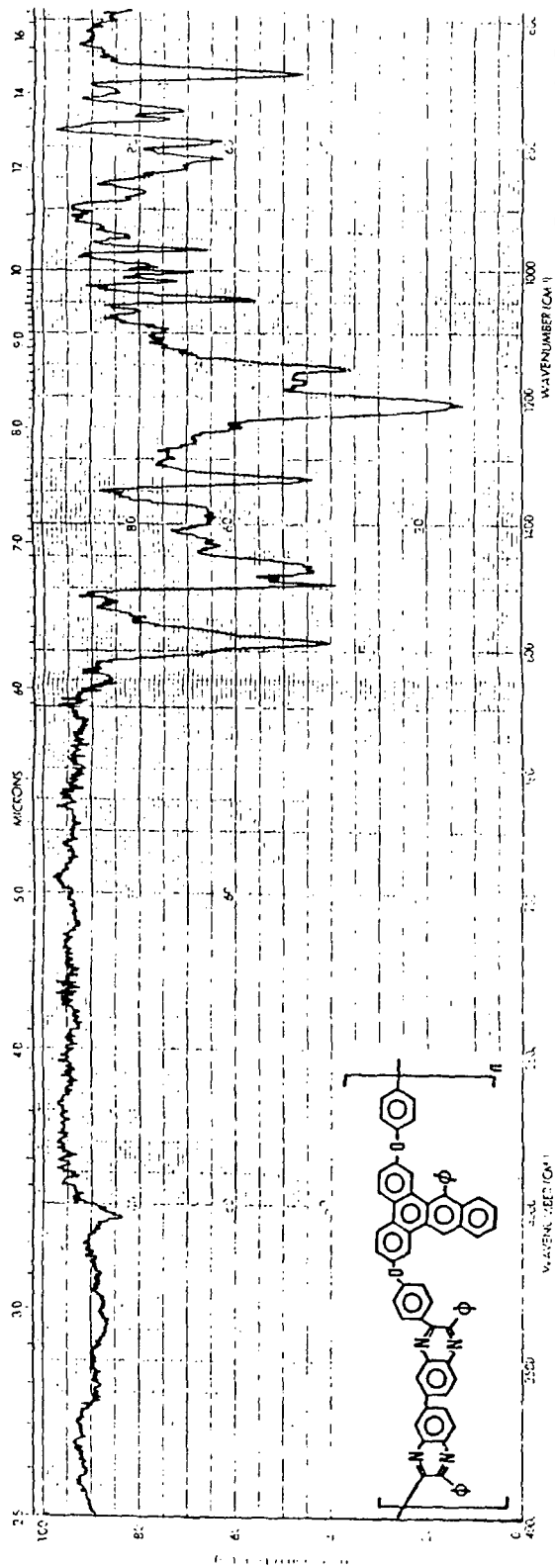


Figure 11. Infrared Spectrum of Closed 4,4'-Quinoxaline Polymer, 17d.

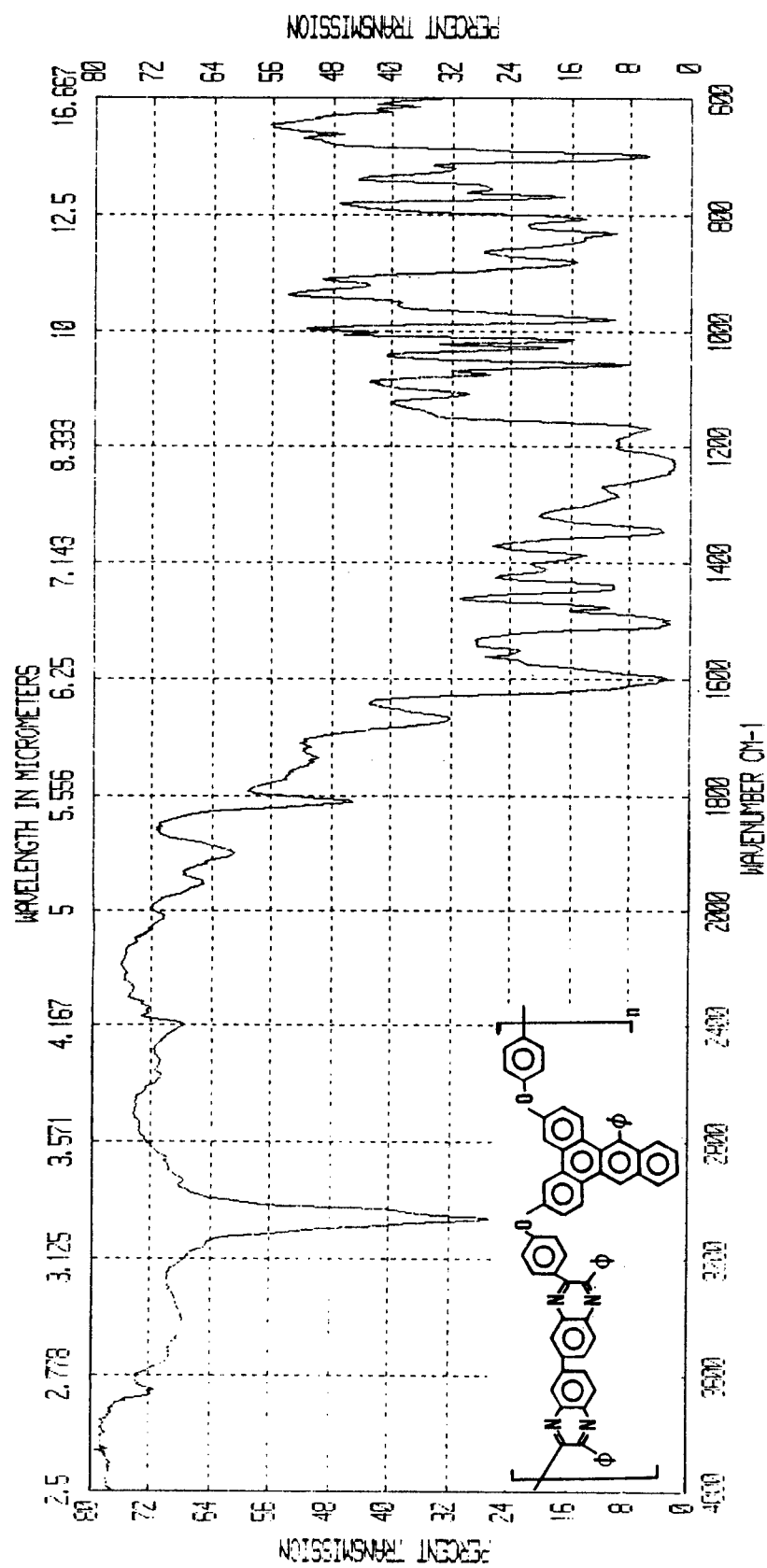


Figure 12. FTIR Spectrum of Cured 5,5'-Quinoxaline Polymer, 17b.

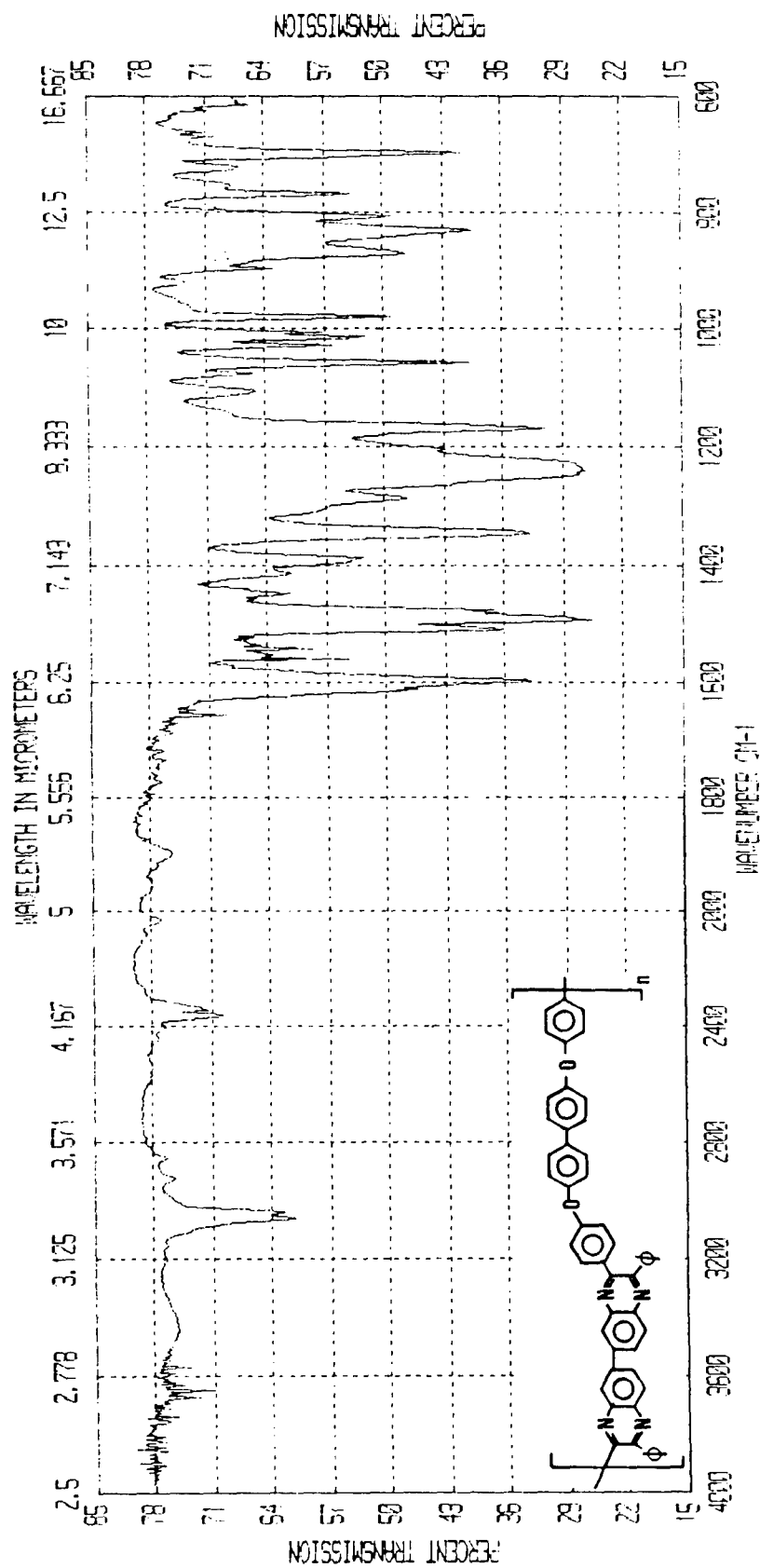


Figure 13. FTIR Spectrum of 4,4'-Quinoxaline Polymer Without Pendants, 17c.

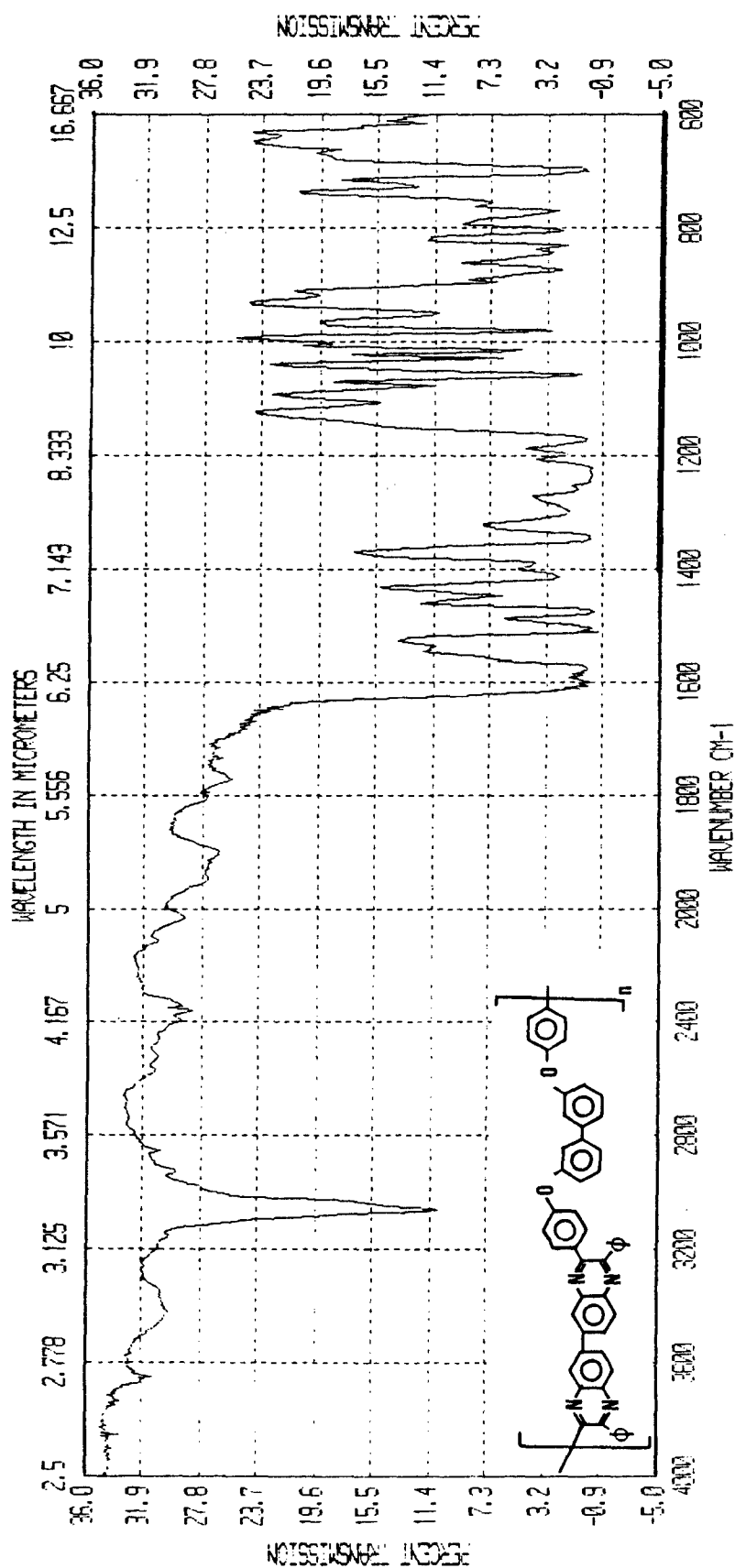


Figure 14. FTIR Spectrum of 3,3'-Quinoxaline Polymer Without Pendant, 17e.

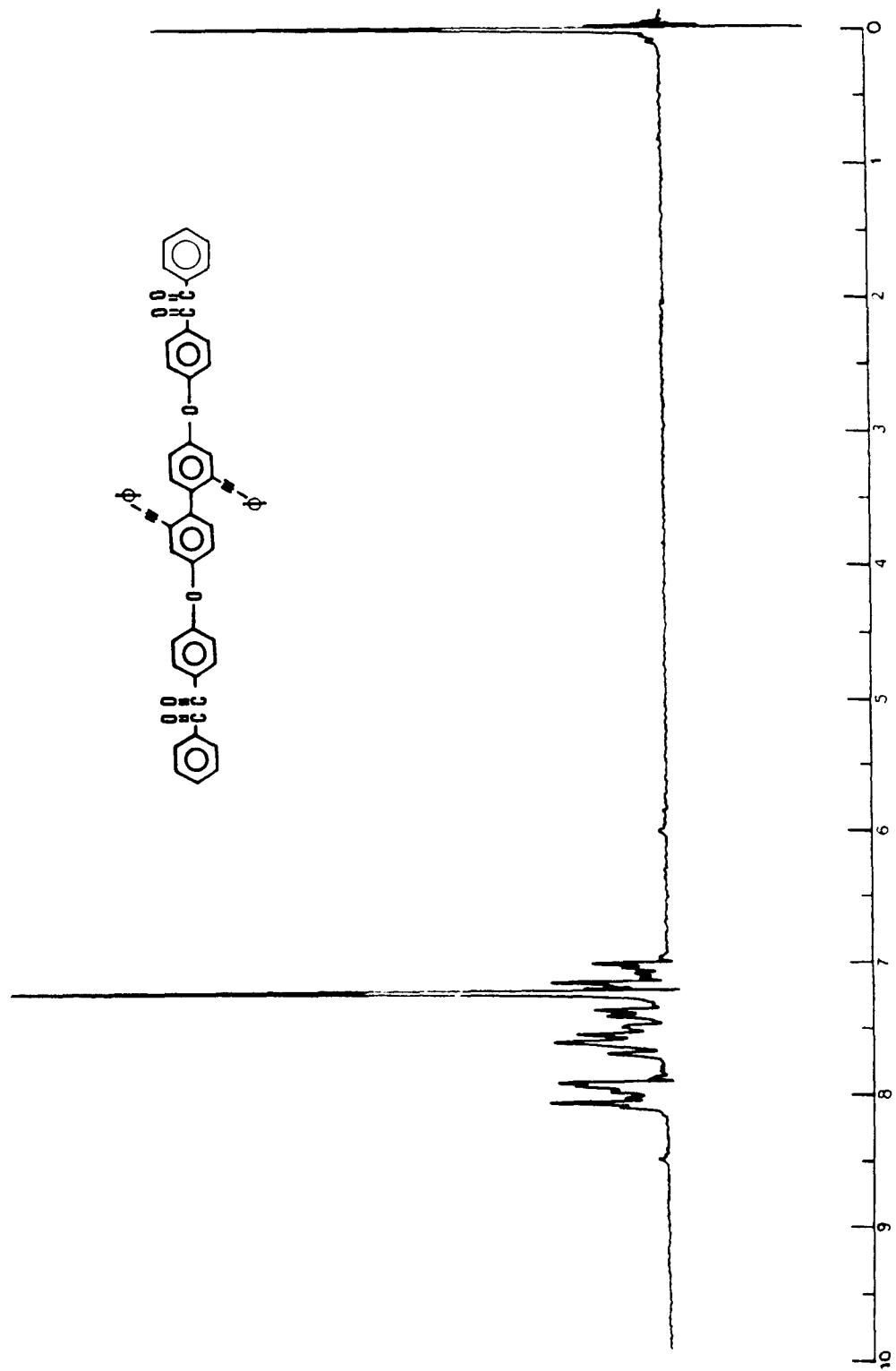


Figure 15. ^1H NMR Spectrum of 4,4'-Bisbenzil Monomer, 3a.

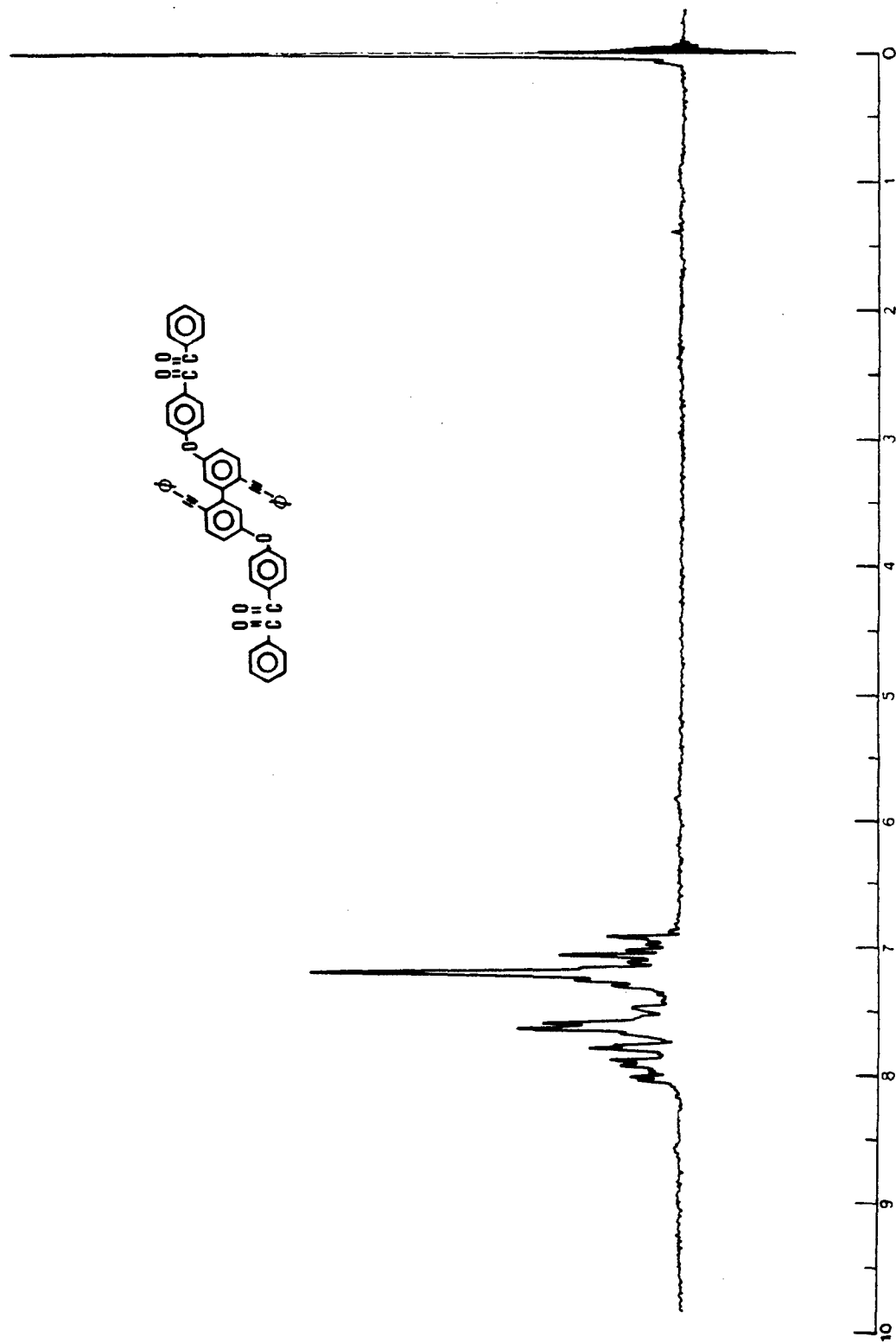


Figure 16. ^1H NMR Spectrum of 5,5'-Bisbenzil Monomer, 3b.

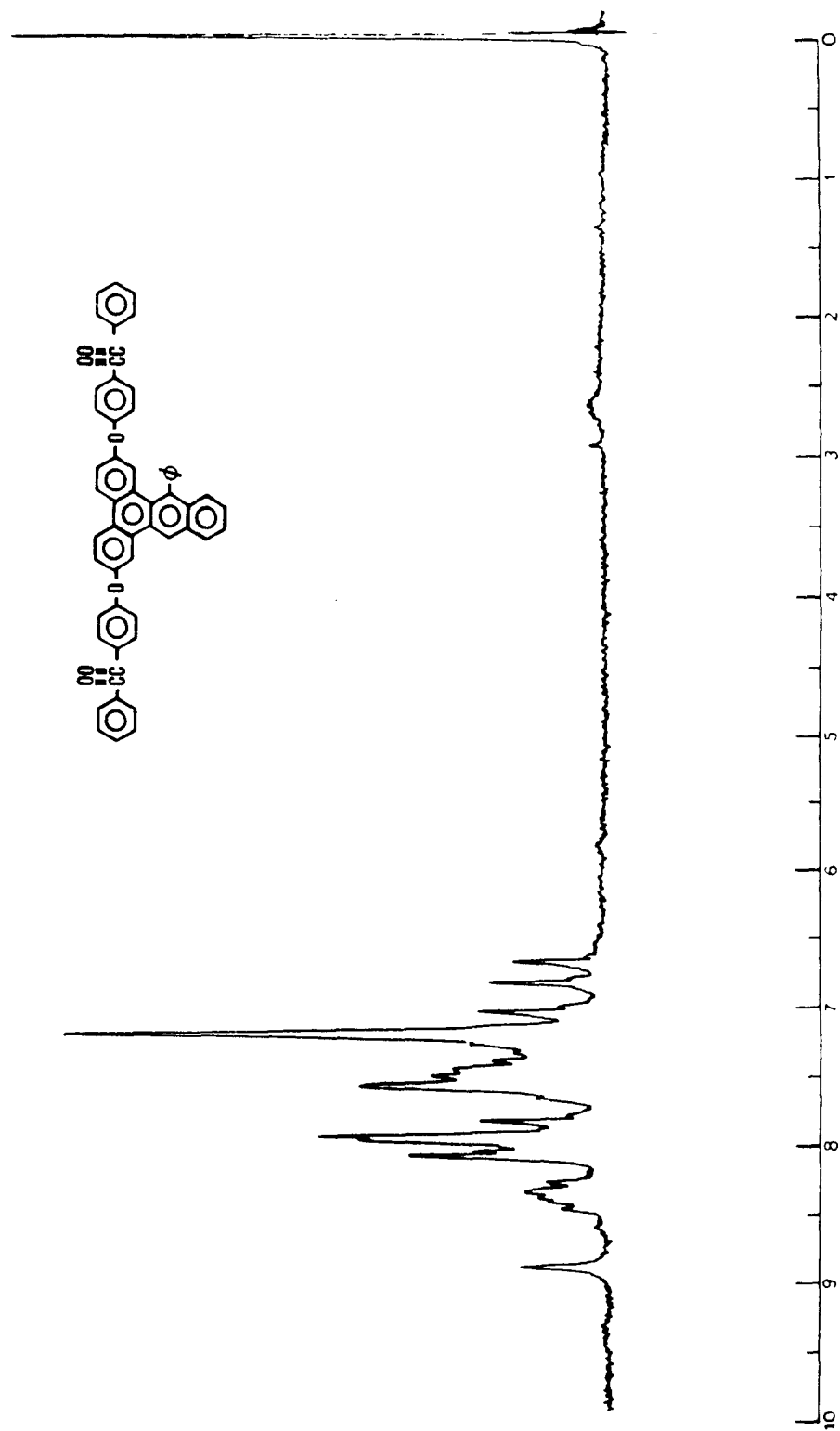


Figure 17. ^1H NMR Spectrum of Closed 4,4'-Bisbenzil Monomer, 3c.

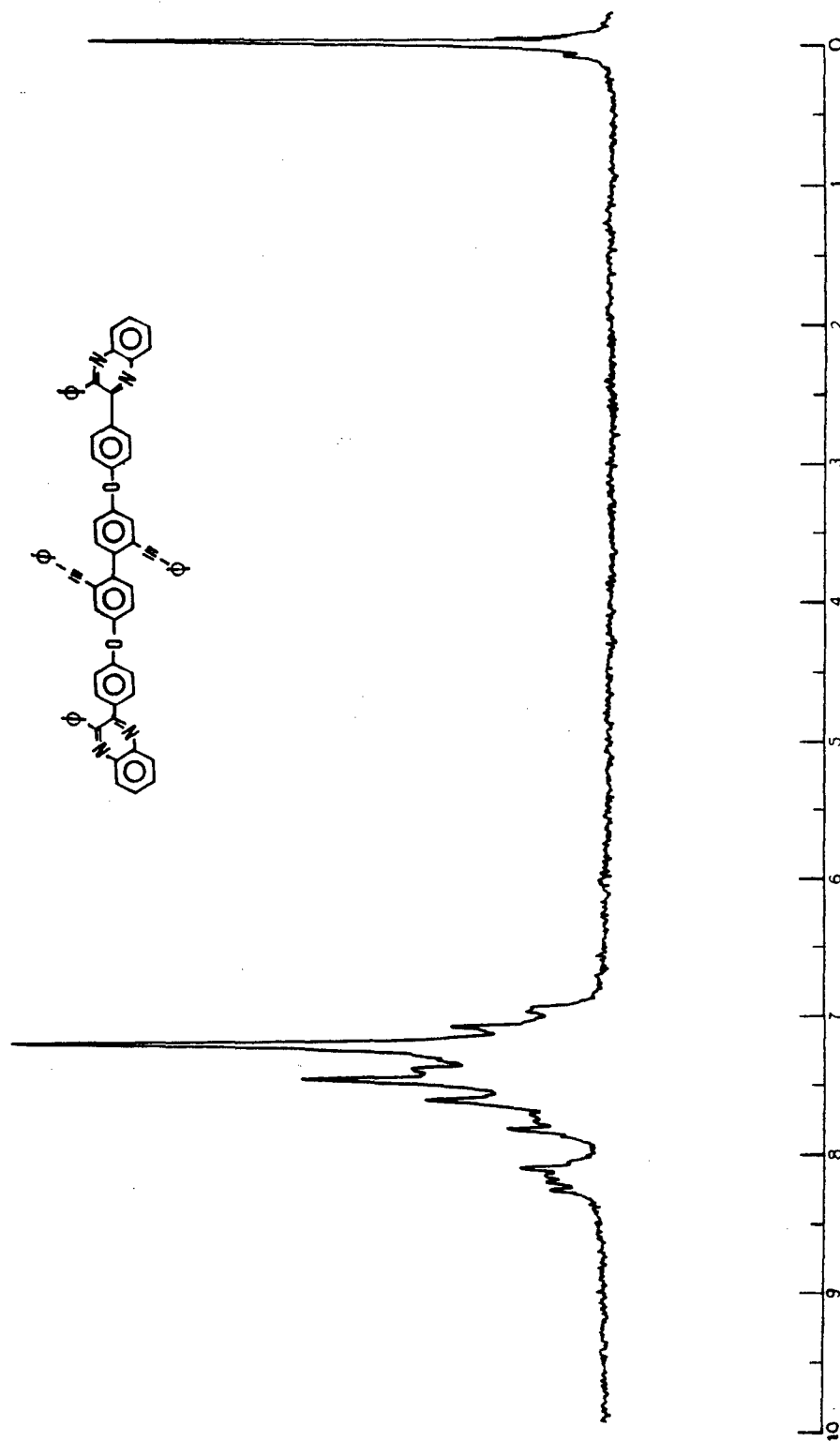


Figure 18. ^1H NMR Spectrum of 4,4'-Quinoxaline Model Compound, 15a.

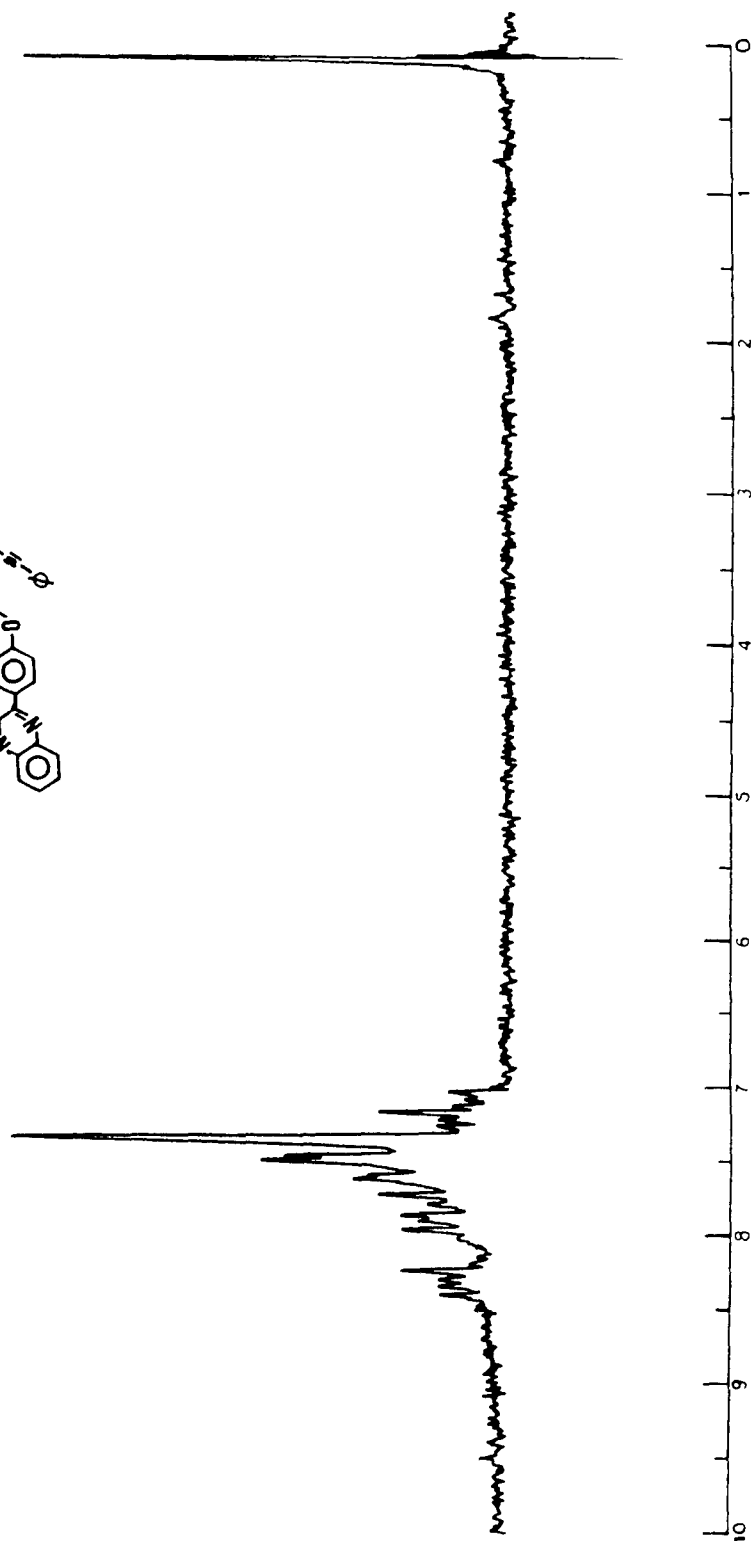
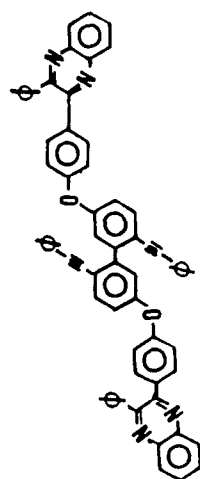


Figure 19. ^1H NMR Spectrum of 5,5'-Quinoxaline Model Compound, 15b.

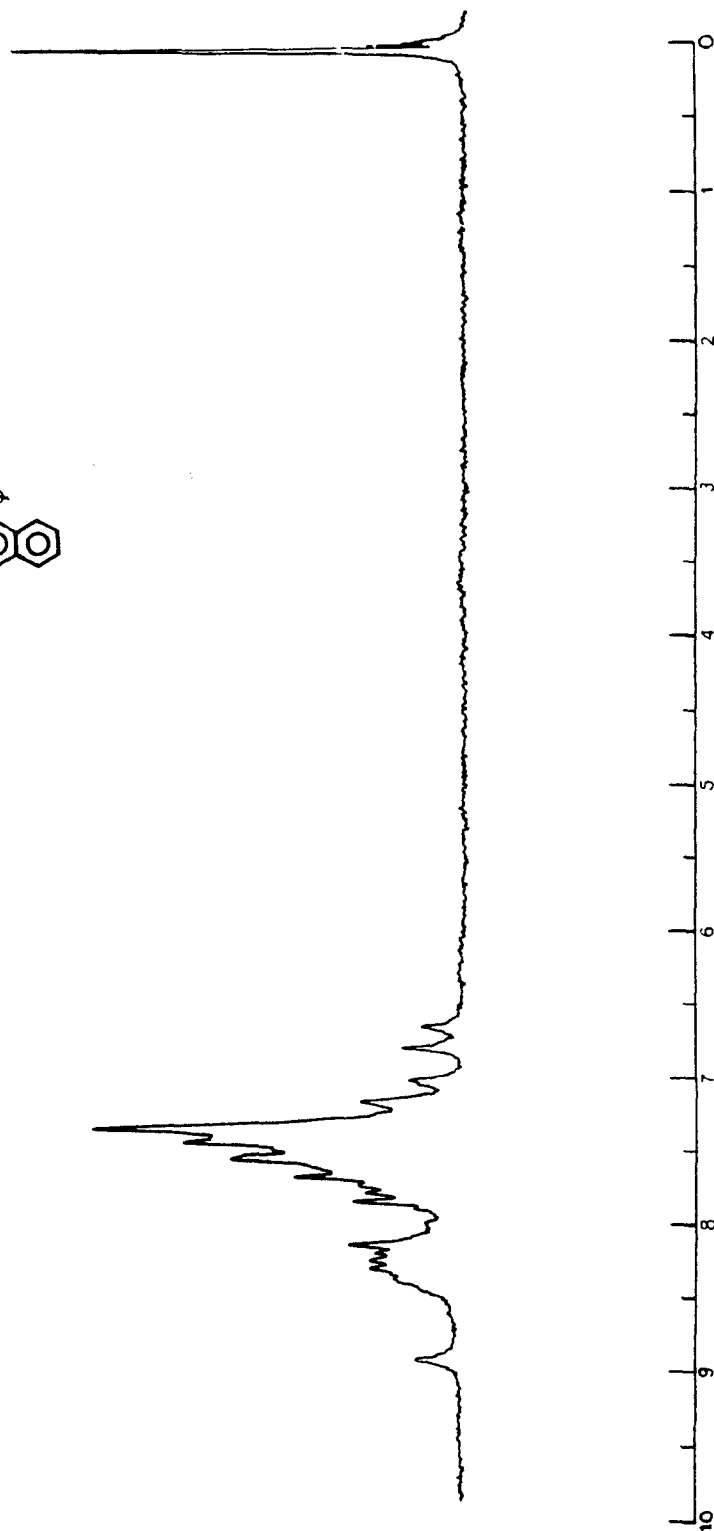
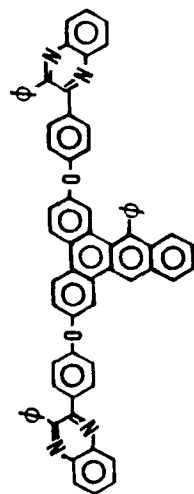


Figure 20. ^1H NMR Spectrum of Closed 4,4'-Quinoxaline Model Compound, 16.

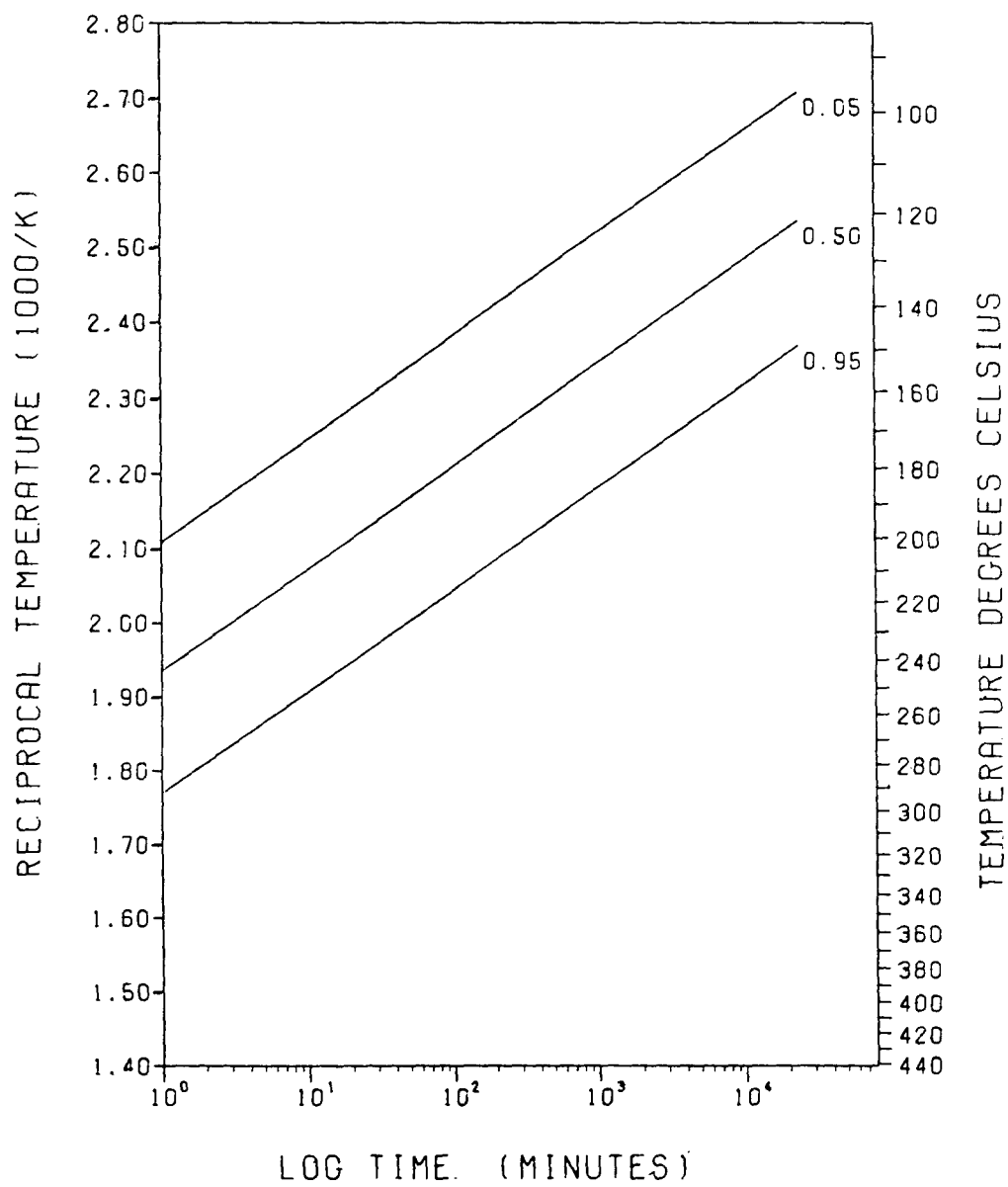


Figure 21. Reaction Window Plot of Polymer 17a.

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